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A study of the dissolution of hafnium in hydrofluoric acid

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A STUDY OF THE DISSOLUTION OF HAFNIUM IN HYDROFLUORIC ACID

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Presented to

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In Partial Fulfillment

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Doctor of Philosophy

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by

James Winston Johnson

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A STUDY OF THE DISSOLUTION OF HAFNIUM IN HYDROFLUORIC ACID

The purpose of this investigation was to obtain kinetic and electrochemical information concerning the reaction of hafnium with hydrofluoric acid in order to establish the mechanism of dissolution. This included the determination of dissolution rates, the difference effect, and dissolution potentials of hafnium in hydrofluoric acid.

The dissolution rates were obtained by a gas evolution method according to the reaction: $Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2$. The hydrofluoric acid concentration was varied from 0.05 to 1.00 N and the temperature from 5 to 50°C. The effect of stirring speed was also studied. It was found that: (1) the Hf-HF reaction is first order with respect to the unionized HF concentration over the range studied, (2) the activation energy for the reaction is 5.3 ± 0.2 kcal/mol, and (3) the reaction rate is directly proportional to the stirring speed in the range 100 to 400 revolutions per minute. It was concluded the dissolution of hafnium in hydrofluoric acid is a diffusion controlled reaction.

Additions of fluoride salts, noble metal salts, oxidizing agents, and mineral acids were made during the dissolution. It was found that: (1) fluoride salts increase the dissolution rate until a critical cation concentration is reached where the reaction is passivated by the formation of insoluble salts on the metal surface; (2) noble metal salt additions, 0.005 N, passivate the reaction by formation of insoluble films (presumably oxide) on the hafnium

surface promoted by reduction of the noble metal ions; (3) oxidizing agents, 0.0529 N, passivate the reaction by promotion of insoluble films (presumably oxide) on the metal surface; and (4) mineral acids, 0.10 N, show no consistent trend, hydrochloric acid additions increase the reaction rate, sulfuric acid additions show no appreciable effect, and phosphoric acid retards the reaction slightly.

Difference effect measurements showed that: (1) the difference effect is directly proportional to the current density and independent of hydrofluoric acid concentration, and (2) anodic currents have a very strong polarizing influence on the dissolution reaction.

The dissolution potential of hafnium became less noble as the hydrofluoric acid concentration was increased. By making additions during the potential studies, it was found that: (1) fluoride salts in concentrations sufficient to give passivation cause the potential to become less noble, (2) noble metal salts, 0.005 N, make the potential more noble, (3) oxidizing agents, 0.0529 N, make the potential less noble, (4) hydrochloric acid, 0.10 N, makes the potential more noble, and (5) sulfuric and phosphoric acid, 0.10 N, show no appreciable effect.

Surface reactions on hafnium are proposed as follows:

1. Initiation of the dissolution reaction by attack on (or diffusion through) the protective oxide layer by unionized HF:

$$HfO_w + 4\ HF \longrightarrow HfF_4 + (2 - w)\ H_2 + w\ H_2O$$

2. Reaction of the metal with H° and H_2O to form surface films:

$$Hf + x\ H^\circ \longrightarrow HfH_x$$

$$Hf + y\ H_2O \longrightarrow HfO_y + y\ H_2$$

3. Dissolution of the metal by HF and H^+ diffusing through the surface films:

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2 \qquad \text{(chemical)}$$

$$Hf + 4\ H^+ \longrightarrow Hf^{+4} + 2\ H_2 \qquad \text{(electrochemical)}$$

Evidence indicates that (1) during the normal dissolution reaction, the hydride is the predominate film formed on the metal surface, and the electrochemical contribution to the total rate is small, and (2) noble metal couples, oxidizing agents, and anodic currents passivate the metal surface by promoting oxide film formation.

The rapid rate of self-dissolution of hafnium is most likely explained by a chemical attack of unionized HF and the rate controlling step is the diffusion of unionized HF to the reacting surface.

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CHAPTER I

INTRODUCTION

The use of relatively pure hafnium on a commercial scale has been accomplished only in the past few years. Its technological development has been closely connected to that of zirconium due to their chemical similarity and their simultaneous occurrence in nature. Zirconium, because of its low neutron absorption cross section and excellent corrosion resistance, is highly desirable as a structural material in water-cooled nuclear reactor cores. Conversely, the presence of hafnium with its high neutron absorption cross section is very undesirable and its practically complete removal is necessary for reactor grade zirconium. This led to production of hafnium as a by-product which at first was stored due to there being no specific use for it. However, the decision in 1951 to use hafnium as a control rod material has led to its extensive use in this field in water cooled reactors.

Hafnium is resistant to a wide variety of chemical corrosives. The only mineral acids that appreciably attack it are hydrofluoric acid, phosphoric acid, concentrated sulfuric acid, and aqua regia. Of these, only hydrofluoric acid attacks the metal with an appreciable rate.[1]

The purpose of this investigation was to establish the mechanism of the dissolution of hafnium in hydrofluoric acid. To accomplish this, a kinetic and electrochemical study of the dissolution

reaction was made. The kinetic study included the dissolution rate, the effect of temperature on the rate, and the effect of various additives on the rate. The electrochemical study included the difference effect, dissolution potentials, and the effect of various additives and current density on the dissolution potentials.

At present, there is no information in the literature available pertaining to the kinetics and electrochemical effects of the dissolution of hafnium in hydrofluoric acid.

CHAPTER II

REVIEW OF LITERATURE

Due to the small amount of literature available on the chemical behavior of hafnium, it is best discussed in conjunction with the elements of Group IVB (titanium group) of the Periodic System--titanium, zirconium, hafnium, and thorium. Some of the properties of these elements are summarized in Table I.

The abundances of the elements of the titanium group are compared to those in the zinc group--zinc, cadmium, and mercury. However, unlike the zinc group metals which are rare but easily isolated, the titanium group metals are abundant but very difficultly purified.

Potentiometrically, the Group IVB metals are better reducing agents than zinc. However, in a manner similar to aluminum, they may exhibit passivity and remain relatively unaffected for long periods of time in contact with concentrated mineral acids at ordinary temperatures.

The Group IVB elements all form hydrides, oxides, sulfides, halides, nitrides, carbides, and borides when treated with the appropriate non-metals at higher temperatures.

The atoms of Ti, Zr, and Hf have two s electrons and two inner d electrons beyond rare gas configuration. All four of these electrons may be involved in oxidation, resulting in the +4 oxidation state characteristic of the group. Ti(III) is also of some

TABLE I

Summary of Properties of the Group IVB Elements.

ELEMENT	Titanium	Zirconium	Hafnium	Thorium
Symbol	Ti	Zr	Hf	Th
Atomic Number	22	40	72	90
Atomic Weight	47.90	91.22	178.50	232.05
Density, gm/cm^3	4.49	6.52	13.31	11.71
Melting Point, °C	1725	2100	2300	1800
Atomic Radius, Å	1.49	1.58	1.57	1.82
Ionic Radius, Å (M^{+4})	0.64	0.87	0.84	1.10
Oxidation Potential, volts	--	1.53	1.70	1.90

Remy, H.: "Treatise on Inorganic Chemistry," Vol. II, p. 44. Elsevier Publishing Co., New York, N. Y., 1956.

importance. Derivatives of Ti(II), Zr(III), and Hf(III) are known, but they are unstable. The elements never function as the electronegative constituents of compounds.[2]

Hafnium and zirconium are almost invariably found together, perhaps having properties more nearly alike than any other pair of elements. It is generally assumed, when there is a lack of other information, that the behavior of zirconium and its compounds may be applied to hafnium.

Quantitative studies pertaining to the dissolution of zirconium in hydrofluoric acid have been reported in the literature. These studies have been made by Baumrucker;[3] Smith and Hill;[4] Straumanis, James, and Neiman;[5] Vander Wall and Whitner;[6] and James, Custead, and Straumanis.[7,8]

Baumrucker followed the reaction rate by the decrease in weight and thickness of the reacting zirconium samples;[3] Smith and Hill[4] and Vander Wall and Whitner[6] made use of radioactive Zr^{95} and a scintillometer to measure the build up of zirconium ions in solution. Straumanis, James, and Neiman[5] and James, Custead, and Straumanis[7,8] followed the reaction by measuring the rate of hydrogen evolution from the reacting metal. There was unanimous agreement that the reaction was first order with respect to molecular HF in concentrations up to 0.5 N HF, and that diffusion of the molecular HF to the metal surface was the rate controlling step. This mechanism was supported by the low activation energies reported (Baumrucker, 4.2 kcal/mol; Smith and Hill, 3.34 kcal/mol; Vander Wall and Whitner,

6.6 kcal/mol; and James, Custead, and Straumanis, 3.8 kcal/mol) and the dependency of the dissolution rate on the liquid velocity across the metal surface. The higher activation energy of Vander Wall and Whitner was observed in HF-HNO_3 solutions. It was postulated by James, et al.,[7] that this was due to the formation of oxide layers on the metal surface promoted by the HNO_3, a strongly oxidizing acid. These oxide layers would further hinder the diffusion of the HF molecules to the metal surface thereby increasing the activation energy.

The excellent corrosion resistance of hafnium has somewhat retarded detailed studies on its corrosion behavior as there was no practical need for them. Studies that have been made and reported in the literature pertain mainly to: (1) hot water corrosion as affected by temperature, nitrogen content, alloy additions, cold working, and irradiation, and (2) high temperature gas-metal reactions with air, oxygen, nitrogen, and hydrogen. These studies were made mainly on crystal bar hafnium containing two to five weight per cent zirconium. Special emphasis was placed on surface preparation of the corrosion samples to obtain reproducible test results.

The information pertaining to hot water corrosion indicates that: (1) upon exposure to water, hafnium forms a protective oxide film that grows very slowly with time, causing a gradual increase in the weight of the tested samples and that the hot water corrosion resistance of hafnium is much superior to that of zirconium,[9] (2) the corrosion resistance of hafnium decreases as the nitrogen content increases, but the resistance is still better than that of the

corresponding zirconium alloy and not as sensitive to nitrogen content,[10] (3) the corrosion resistance of hafnium-titanium alloys reaches a minimum at approximately ten weight per cent titanium, then rapidly increases to values comparable to non-alloyed hafnium,[11] (4) significant amounts of cold work on hafnium cause no harmful consequences to its corrosion resistance,[12] and (5) the corrosion resistance of hafnium is not adversely affected by exposure to radiation.[13]

The information pertaining to the gas-metal reactions indicates that: (1) hafnium has excellent resistance to air at elevated temperatures and can be hot-worked at 900°C without protection,[14] (2) the oxidation of hafnium between 350°C and 1200°C with oxygen pressures of 760 mm Hg follows the "accepted laws of oxidation, i.e., successive logarithmic, parabolic, and linear rate laws, with activation energies of 11.4, 36.0, and 26.1 kcal/mol, respectively,[15] and (3) the reaction of hafnium with nitrogen at temperatures between 876°C and 1034°C with nitrogen pressures from 38 to 402 mm Hg follows the parabolic rate law with an activation energy of about 57 kcal/mol.[16]

A limited amount of information is available on the corrosion behavior of hafnium in various chemical media. A summary of this information is presented in Table II allowing a direct comparison of the corrosion rates of hafnium, zirconium, and titanium.

TABLE II

Corrosion Rate of Hafnium, Zirconium, and Titanium in Various Media at 35°C.

Corrosion Medium	Corrosion Rate of Hf	Corrosion Rate of Zr	Corrosion Rate of Ti
	inches/year	inches/year	inches/year
H_2SO_4 (96.2%)	soluble	soluble	soluble
H_2SO_4 (10%)	3.5×10^{-4}	0.36×10^{-4}	3.2×10^{-4}
HCl (37%)	13×10^{-4}	6.1×10^{-4}	soluble
HCl (10%)	3.5×10^{-4}	0.12×10^{-4}	2.5×10^{-4}
HNO_3 (fuming)	4.4×10^{-4}	gains weight	gains weight
HNO_3 (69.7%)	1.8×10^{-4}	gains weight	8.64×10^{-4}
HNO_3 (10%)	3.5×10^{-4}	0.12×10^{-4}	1.2×10^{-4}
$HCl-HNO_3$ (1:1)	0.13	slowly attacked	3.9×10^{-4}
$HCl-H_2SO_4$ (1:1)	4.8×10^{-4}	0.79×10^{-4}	soluble
$HNO_3-H_2SO_4$ (1:1)	0.19	0.0865	48×10^{-4}
NaOH (50%)	1.8×10^{-4}	gains weight	3.5×10^{-4}
NaCl (20%)	0.88×10^{-4}	0.24×10^{-4}	0.18×10^{-4}

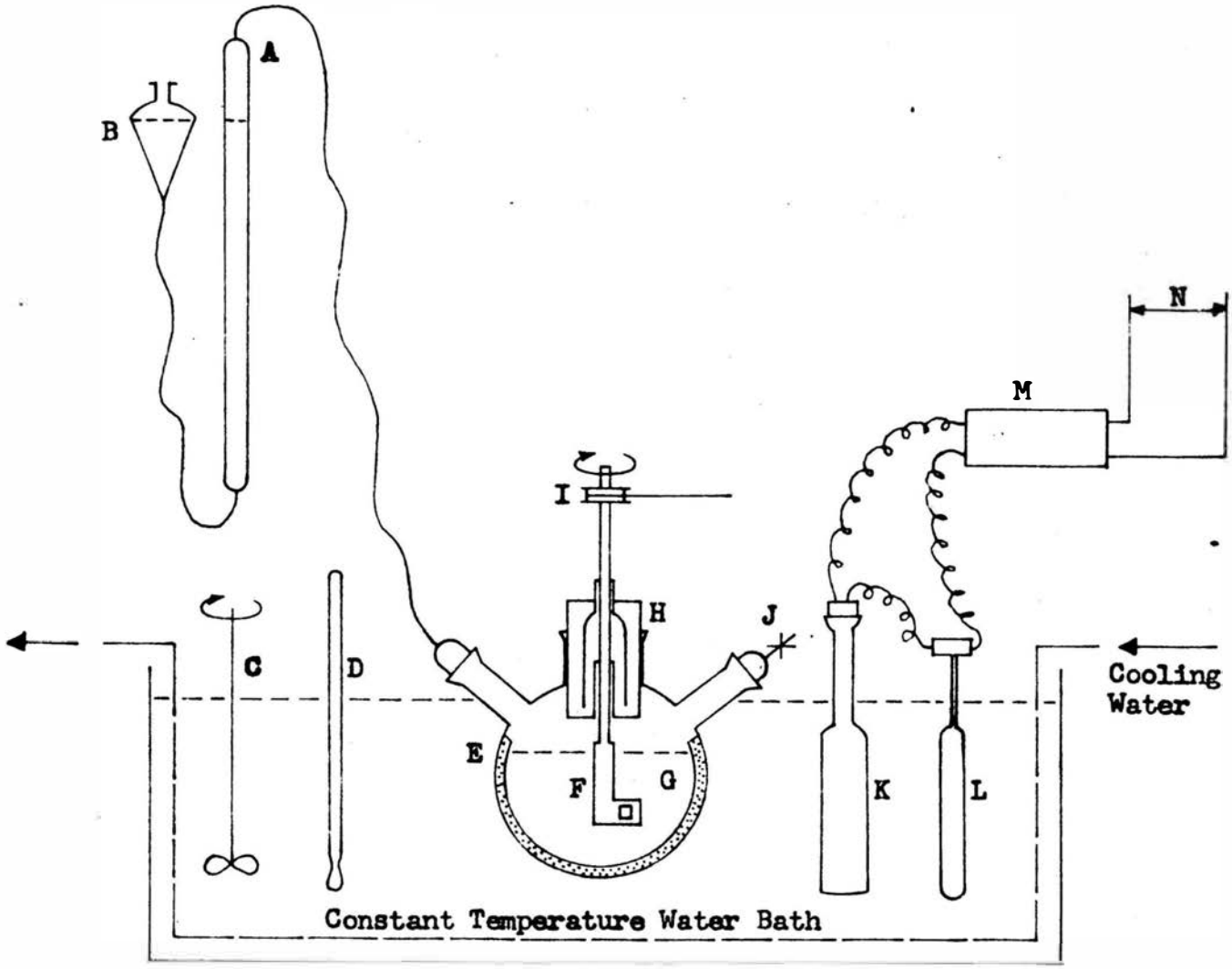
Everhart, J. L.: Hafnium Metal--Its Properties and Future, Materials and Methods, 36, 95 (1952);
Chirigos, J. N.: Corrosion of Hafnium, "The Metallurgy of Hafnium," p. 271. Naval Reactors, USAEC, Washington, D. C.

CHAPTER III

EXPERIMENTAL

The purpose of this investigation was to obtain kinetic and electrochemical information concerning the reaction of hafnium with hydrofluoric acid in order to establish the mechanism of dissolution. Specifically, this included: (1) the dissolution rate of hafnium, (2) the effect of temperature on the dissolution rate, (3) the effect of various additives on the dissolution rate, (4) the difference effect for the dissolution, (5) the dissolution potentials, and (6) the effect of various additives and current density on the dissolution potentials.

The plan of experimentation was divided into three distinct phases. Phase I: Measurement of the dissolution rate of hafnium as affected by hydrofluoric acid concentration, temperature, and various additives. This was accomplished indirectly by measuring the rate at which hydrogen gas was evolved using apparatus as illustrated in Figure 1. The dissolution rate of hafnium could then be calculated from the hydrogen evolution rate by using stoichiometric relationships. Phase II: Measurement of the difference effect on hafnium dissolving in hydrofluoric acid. This was accomplished by measuring the dissolution rate with and without an anodic current flowing with the use of apparatus as illustrated in Figure 2. The amount of current flowing was measured directly, but again the dissolution rate was followed by the hydrogen evolved. Phase III: The measurement of the dissolution



A - Gas burette
B - Leveling bulb
C - Water bath stirrer
D - Thermometer
E - 500 ml wax-lined flask
F - PVC stirrer foot
G - Hf sample (1 cm^2)
H - Mercury seal
I - Pulley for rotating stirrer
J - Stopcock
K - Knife-blade heater
L - Mercury thermoregulator
M - Relay switch
N - 115 volt A.C. source

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Figure No. 1. Diagram of Apparatus Used for Measurement of Dissolution Rates of Hafnium.

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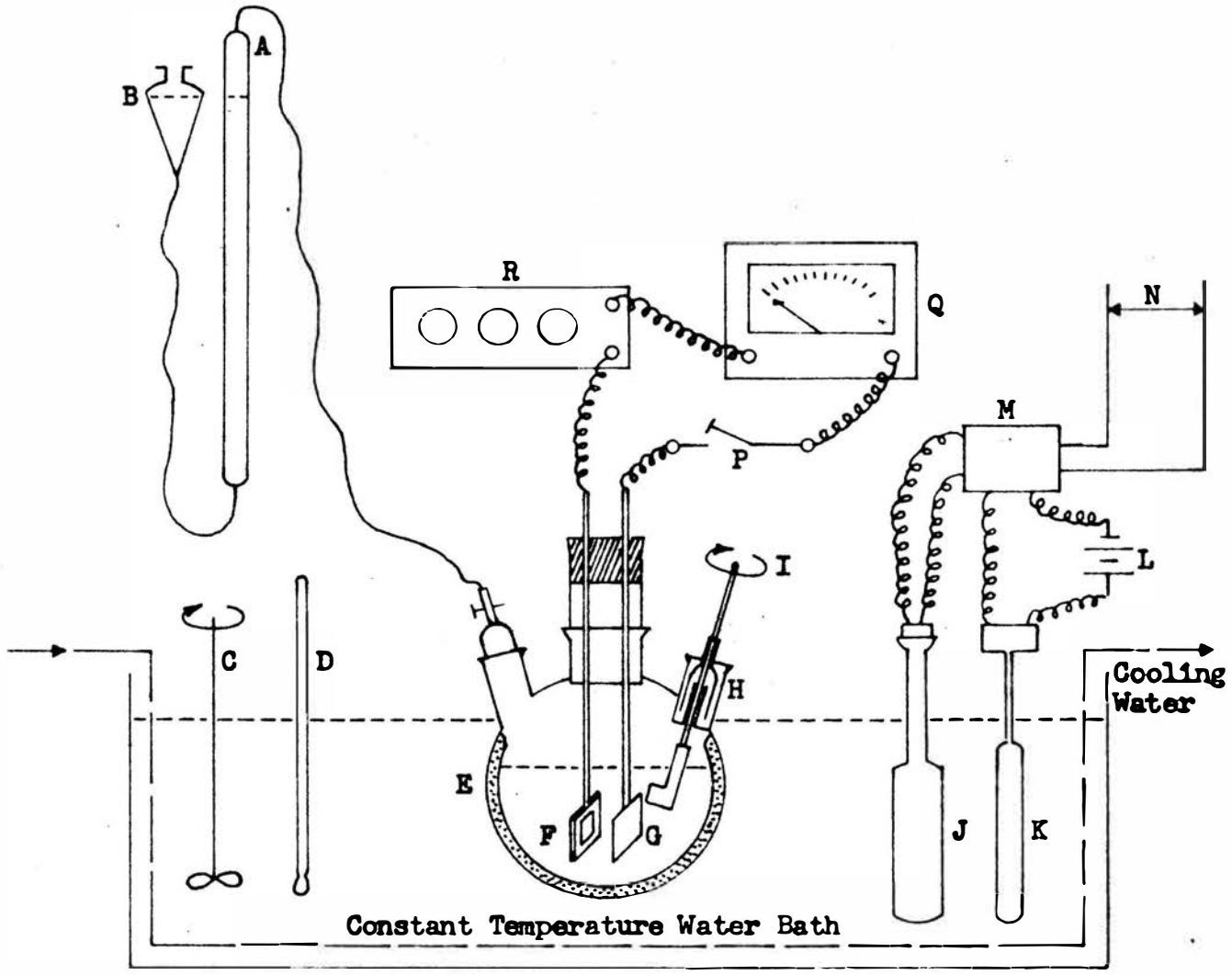

A - Gas burette
B - Leveling bulb
C - Water bath stirrer
D - Thermometer
E - 500 ml wax-lined flask
F - Hf electrode (1 cm^2)
G - Platinized platinum electrode
H - Mercury seal
I - Reactor stirrer
J - Knife-blade heater
K - Mercury thermoregulator
L - 6 volt battery
M - Relay switch
N - 115 volt A.C. source
P - Knife-blade switch
Q - Milli-ammeter
R - Variable resistance box

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Figure No. 2. Diagram of Apparatus Used for Measurement of the Difference Effect for the Dissolution of Hafnium.

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potentials of hafnium in hydrofluoric acid and the effect of various additives and current density on them. These were measured directly with an apparatus as illustrated in Figure 3.

A complete discussion of each of the individual phases, including apparatus, procedure, results, and sample calculations, is presented in this section.

I. MATERIALS

A list of the materials used in this investigation is presented in Appendix A, pages 97 to 100.

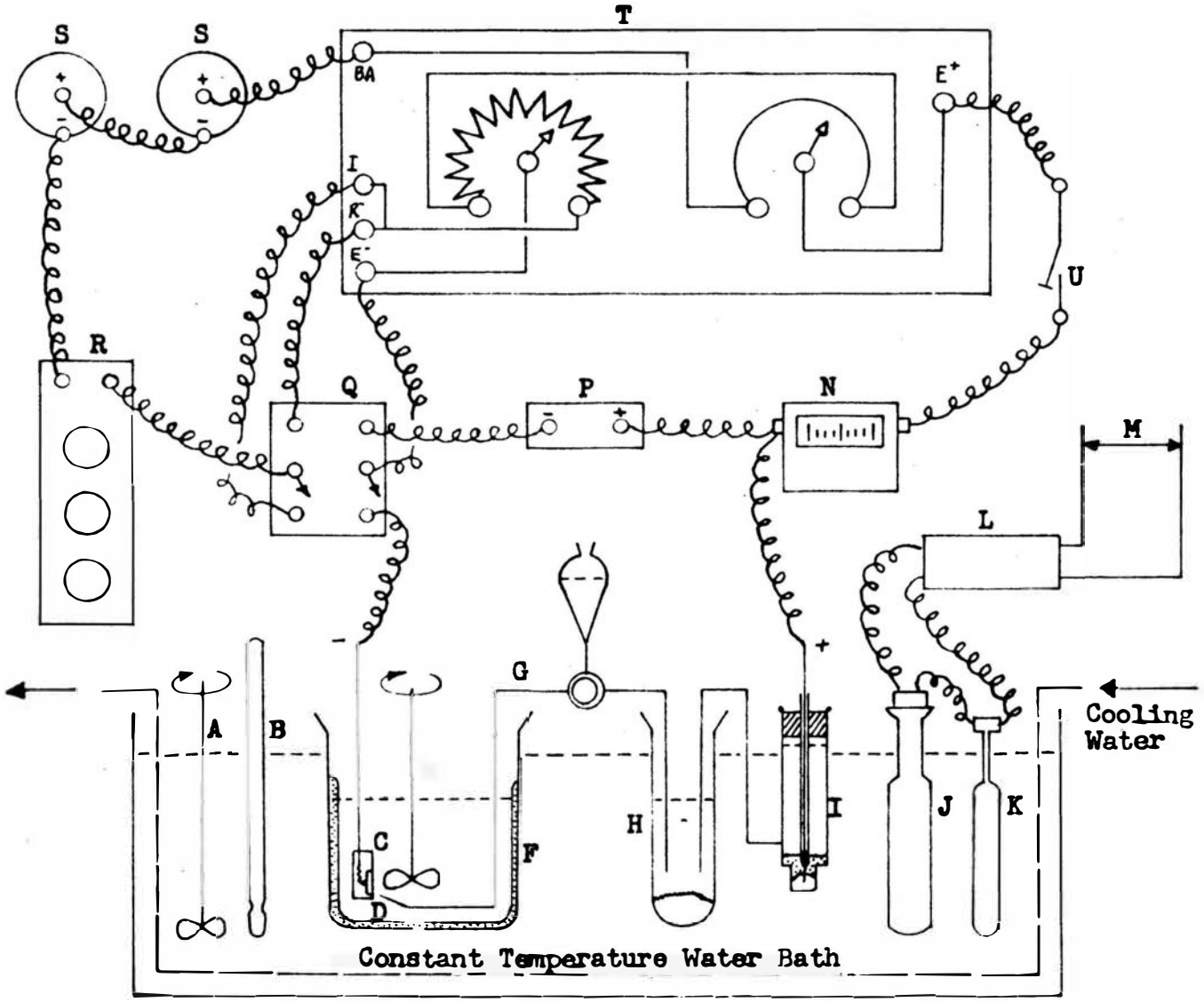
II. APPARATUS

A list of the apparatus used in this investigation is presented in Appendix B, pages 101 to 105.

III. PHASE I OF THE EXPERIMENTAL INVESTIGATION

Measurement of the Dissolution Rate of Hafnium in Hydrofluoric Acid and Hydrofluoric-Hydrochloric Acid Mixture

Apparatus. Figure 1, page 10, shows a diagram of the apparatus used for this part of the experimentation. A description of the individual components of the apparatus is located in Appendix B, pages 101 to 105. The principle of operation of the apparatus was measurement with a gas burette of the volume increase of the gases in the system at specified time intervals. The increase in volume of the gases was due to the hydrogen evolved from the reaction between



A - Water bath stirrer
B - Thermometer
C - Hf Electrode (1 cm^2)
D - Capillary tip
E - Reactor stirrer
F - 600 ml wax-lined beaker
G - 0.14 N HF bridge
H - Saturated KCl solution
I - 1 N calomel electrode
J - Knife-blade heater
K - Mercury thermoregulator
L - Relay switch
M - 115 volt A.C. source
N - Galvanometer
P - Weston cadmium cell
Q - Double-throw switch
R - Variable resistance box
S - 1.5 volt dry cell
T - Potentiometer
U - Key switch

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Figure No. 3. Diagram of Apparatus Used for Measurement of Dissolution Potentials of Hafnium.

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hafnium and hydrofluoric acid.[1] The temperature and pressure at which the gas volume was measured were recorded. Using this data, the rate of hydrogen evolution at standard temperature and pressure was calculated. This rate was used throughout the investigation to indicate the rate of dissolution of the hafnium. The actual rate of hafnium going into solution could be calculated, if desired, by using the stoichiometric relationship between the evolved hydrogen and the dissolved hafnium.

Procedure. A detailed step-by-step procedure for this part of the experimentation is given in Appendix C, pages 107 to 110.

Data and Results. The data from this part of the experimentation are presented in Appendix D, pages 122 to 152.

In this type of reaction, the velocity of the liquid across the reacting surface may influence the dissolution rate. The effect of stirrer speed on the rate in 0.301 N HF-1.00 N HCl acid mixture was studied and the results are shown in Figure 4. The hydrogen evolution rate was found to be proportional to the stirrer speed and can be represented by the following empirical expression in the range of stirrer speeds from 90 to 400 revolutions per minute:

$$dV/dt = 0.00215\ S + 0.665 \qquad (1)$$

where,

dV/dt = hydrogen evolution rate, $ml \cdot cm^{-2} \cdot min^{-1}$

S = stirrer speed, revolutions per minute.

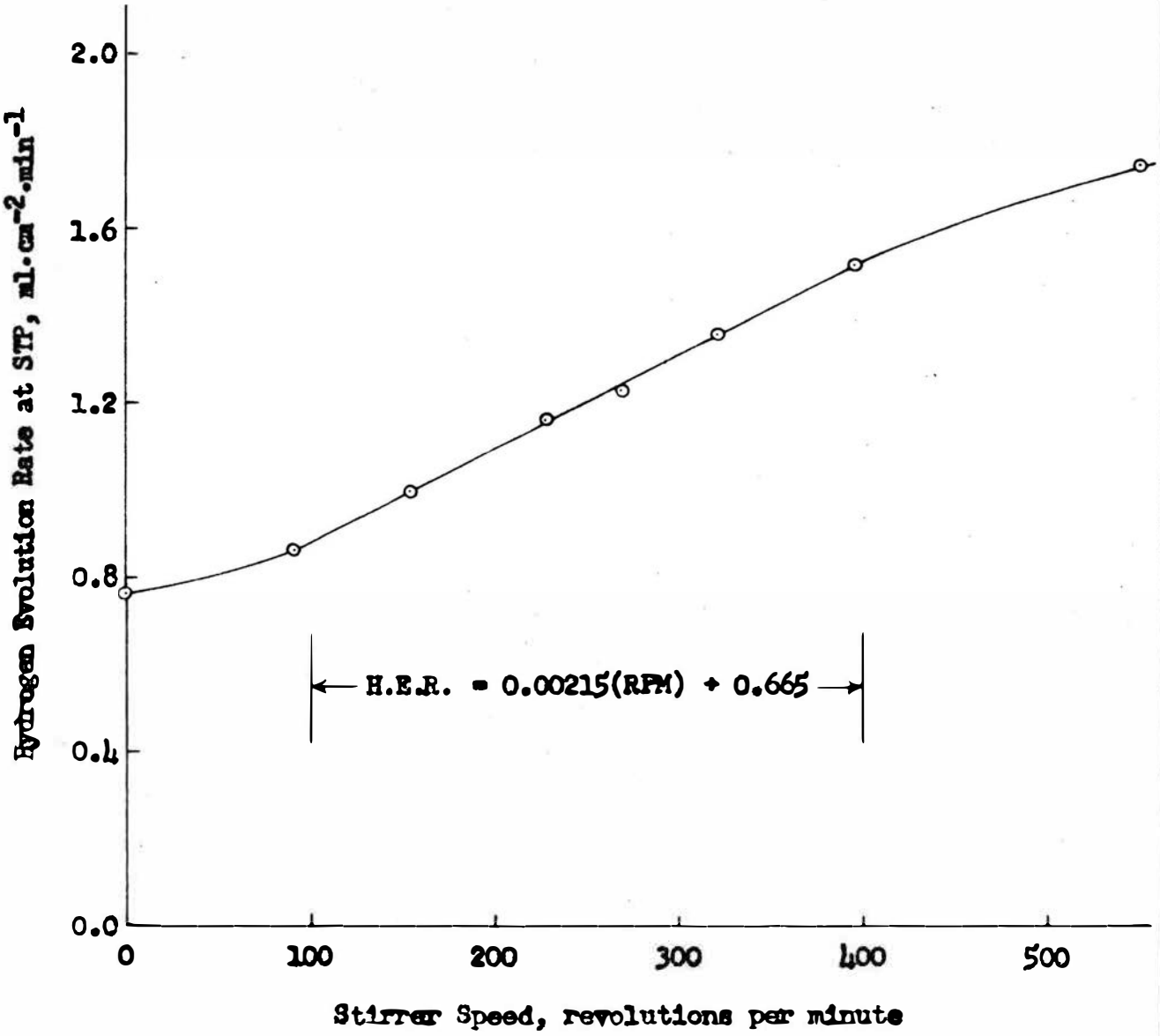

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Figure No. 4. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.301 M Hydrofluoric and 1.00 M Hydrochloric Acid Mixture at 30°C.

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A stirrer speed of 200 revolutions per minute was selected for this investigation so that the results could be compared with those of previous studies on zirconium and titanium made at this stirrer speed in similar equipment.

The average maximum rates were calculated from the data by using the expression:

$$dV/dt = dv/(A\ dt) \qquad (2)$$

where,

dV/dt = hydrogen evolution rate, $ml \cdot cm^{-2} \cdot min^{-1}$

dv = hydrogen evolved, ml at STP

dt = time for hydrogen to be evolved, minutes

A = area of the hafnium surface, cm^2.

The stoichiometry established by Straumanis and Ballass for the dissolution of hafnium in hydrofluoric acid is:[1]

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2 \qquad (3)$$

From this equation, 178.5 grams of hafnium is equivalent to 44.828 liters of hydrogen at STP, or one milliliter of hydrogen at STP is equivalent to 3.98 milligrams of hafnium. Therefore, Equation 2 may be multiplied by this factor to give the rate in terms of milligrams of hafnium, if desired.

Tables III and IV, pages 17 and 18, and Figures 5 and 6, pages 19 and 20, show hydrogen evolution rates versus HF concentration for both hydrofluoric acid and hydrofluoric-1.00 N hydrochloric acid mixtures. The hydrochloric acid was used to control the equilibrium concentrations of fluoride complexes such as HfF_3^{+1},

TABLE III

Hydrogen Evolution Rate for the Dissolution of Hf Metal in Hydrofluoric Acid.

HF Conc.	Hydrogen Evolution Rate - ml/min at STP									
mol HF / liter	5°C		15°C		25°C		35°C		45°C	
0.050					0.0976 0.0960	0.0968*				
0.100	0.106 0.106	0.106*	0.146 0.148	0.147*	0.209 0.212 0.217	0.213*	0.275 0.274	0.274*	0.366 0.370 0.357	0.364*
0.500					1.10	1.10*				

* Average Rate

TABLE IV

Hydrogen Evolution Rate for the Dissolution of Hf Metal in HF-HCl Acid Mixture.

HF Conc.	Hydrogen Evolution Rate - ml/min at STP									
$\frac{\text{mol (HF)}}{\text{liter}}$ un	10°C		20°C		30°C		40°C		50°C	
0.050	0.105 0.100	0.102*	0.125 0.135 0.132 0.128	0.130*	0.157 0.164 0.172	0.164*	0.218 0.213	0.216*	0.300 0.273 0.286	0.286*
0.100	0.211 0.196	0.204*	0.285 0.262 0.254	0.267*	0.348 0.371	0.360*	0.466 0.449	0.458*	0.610 0.594 0.576	0.593*
0.303	0.567 0.578	0.572*	0.839 0.823	0.831*	1.086 1.066	1.08*	1.476 1.419	1.45*	1.842 1.778	1.81*
0.503	1.020 1.017	1.02*	1.424 1.342	1.38*	1.840 1.789	1.81*	2.563 2.512	2.54*	3.186 3.107	3.15*
1.00	2.109 2.180	2.14*	2.954 2.830	2.89*	3.410 3.641	3.53*	5.126 4.902	5.01*	6.783 7.077	6.93*

* Average Rate.

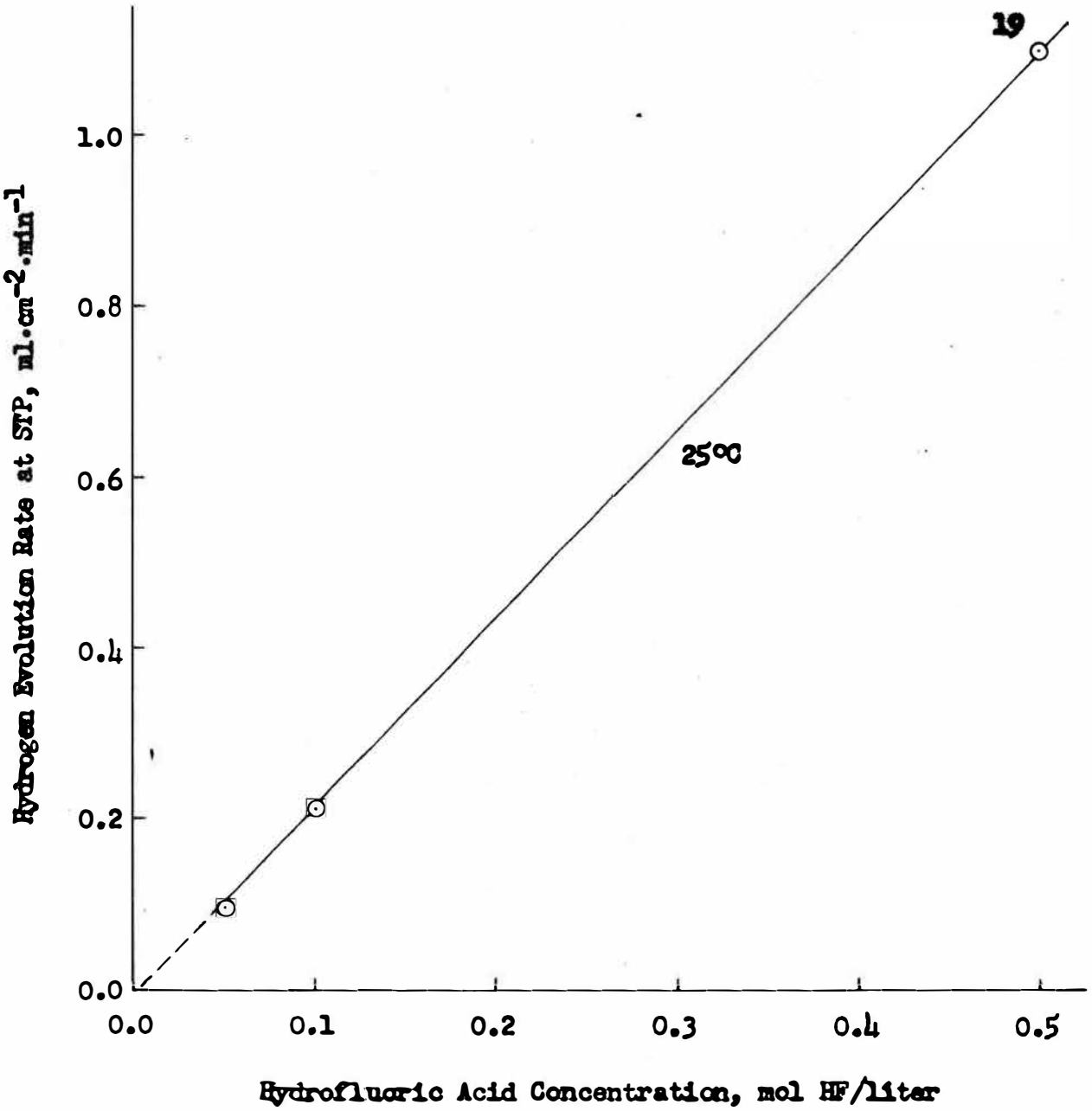

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Figure No. 5. Hydrogen Evolution Rate for the Dissolution of Hafnium in Hydrofluoric Acid.

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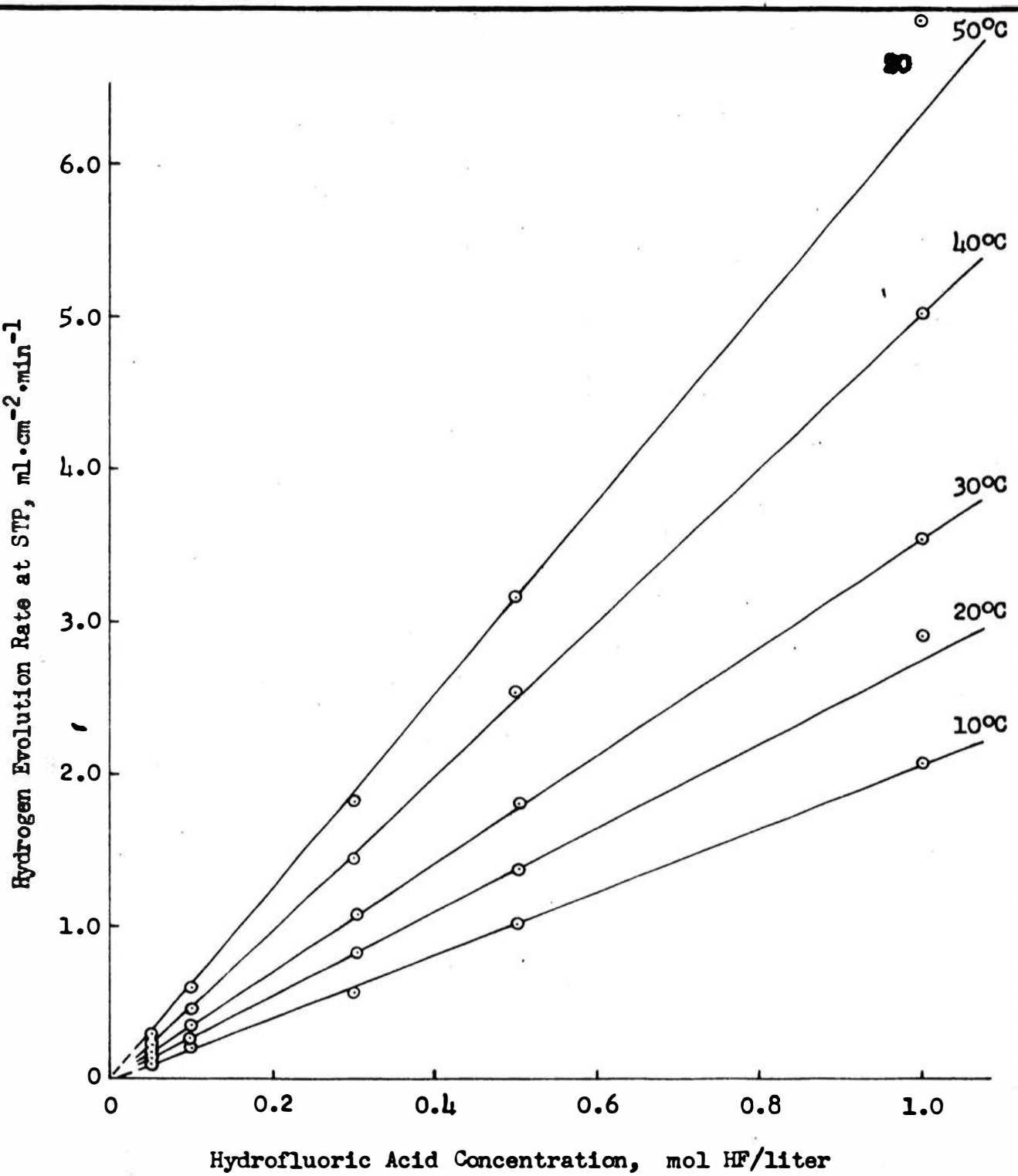

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Figure No. 6. Hydrogen Evolution Rate for the Dissolution of Hafnium in Hydrofluoric and 1.00 N Hydrochloric Acid Mixture.

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HfF_5^{-1}, HfF_6^{-2}, and HfF_7^{-3}. It can be seen from the figures that the plots resulted in straight lines which upon extrapolation passed through the origin. This indicates that the rate is proportional to the HF concentration alone, and accordingly, the form of the rate equation was assumed to be:

$$dV/dt = k\,(HF)^n \qquad (4)$$

where,

dV/dt = hydrogen evolution rate, $ml \cdot cm^{-2} \cdot min^{-1}$

k = reaction rate constant

HF = hydrofluoric acid concentration, mols/l

= unionized HF concentration (approximately)

n = order of the reaction.

Logarithmic plots were made of the hydrogen evolution rate versus HF concentration. The data used to make the plots are shown in Tables V and VI, pages 22 and 23. The plots are shown in Figures 7 and 8, pages 24 and 25. These plots yielded straight lines indicating that the rate equation could be expressed in the form of Equation 4. The slopes of the lines were calculated, giving orders of n from 1.00 to 1.04. This indicates, within experimental error, that the reaction is first order.

Sample Calculations. The following illustrates the calculation of the average maximum hydrogen evolution rate at STP (0°C and 760 mm Hg) for one run at a particular temperature and HF concentration. The data for these calculations were taken from Table XLI, page 153.

TABLE V

Hydrogen Evolution Rate for the Dissolution of Hf Metal in Hydrofluoric Acid.

HF Conc.	Hydrogen Evolution Rate - ml/min at STP				
mol HF / liter	5°C	15°C	25°C	35°C	45°C
0.050 -1.301*			0.0968 -1.014*		
0.100 -1.000*	0.106 -0.975*	0.147 -0.833*	0.213 -0.672*	0.274 -0.562*	0.364 -0.439*
0.500 -0.301*			1.10 +0.041*		

* Logarithm of the corresponding number.

TABLE VI

Hydrogen Evolution Rate for the Dissolution of Hf Metal in HF-HCl Acid Mixtures.

HF Conc. $\frac{\text{mol (HF)}}{\text{liter}}$ un	Hydrogen Evolution Rate - ml/min at STP				
	10°C	20°C	30°C	40°C	50°C
0.050 -1.301*	0.102 -0.991*	0.130 -0.886*	0.164 -0.785*	0.216 -0.666*	0.286 -0.544
0.100 -1.000*	0.204 -0.690*	0.267 -0.573*	0.360 -0.444*	0.458 -0.339*	0.593 -0.227
0.303 -0.519*	0.572 -0.243*	0.831 -0.080*	1.08 +0.033*	1.45 +0.161*	1.81 +0.258*
0.503 -0.298*	1.02 +0.009*	1.38 +0.140*	1.81 +0.258*	2.54 +0.405*	3.15 +0.498*
1.00 0.000*	2.14 +0.330*	2.89 +0.461*	3.53 +0.548*	5.01 +0.700*	6.93 +0.841*

* Logarithm of the corresponding number.

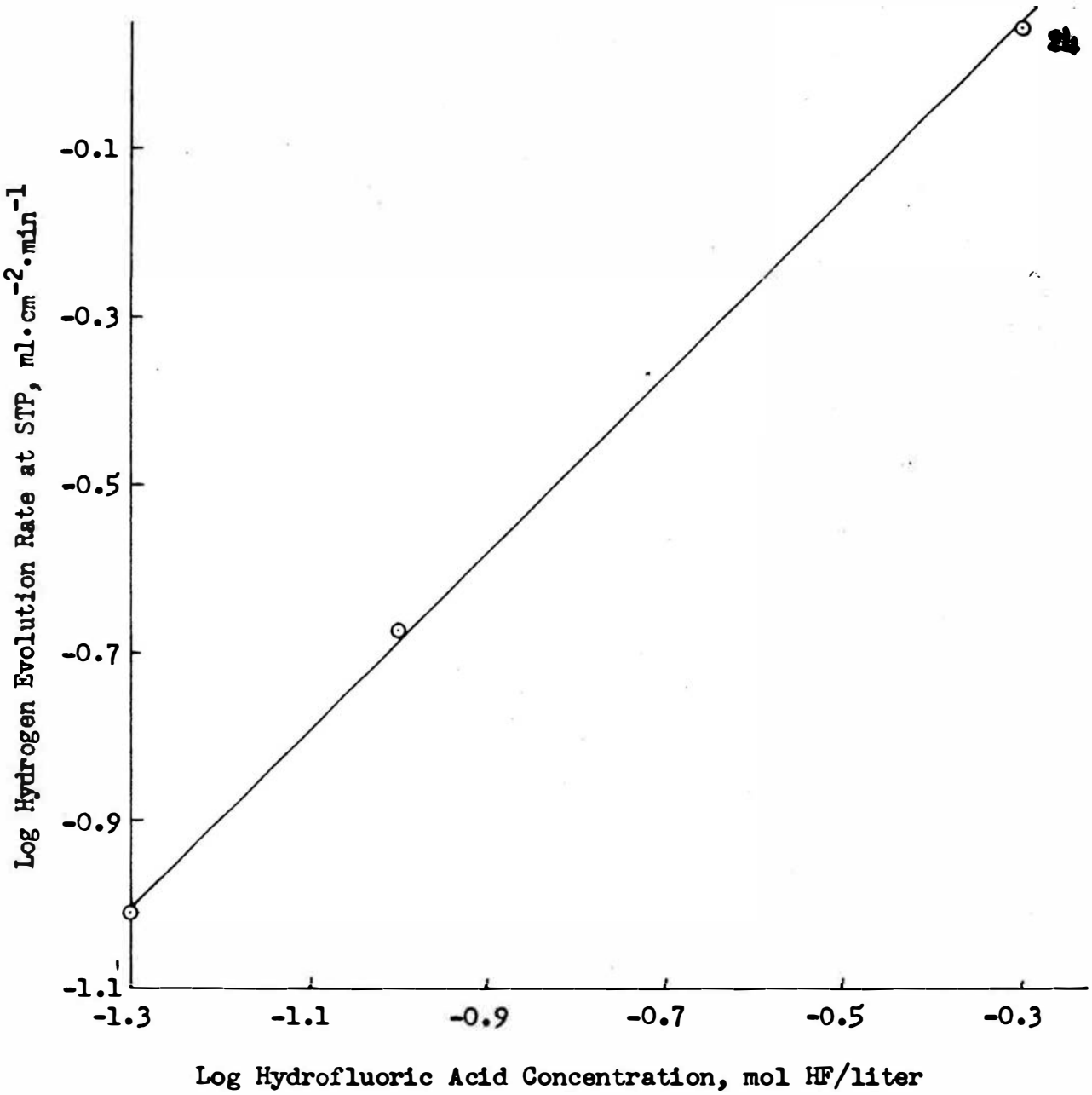

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Figure No. 7. Hydrogen Evolution Rate for the Dissolution of Hafnium in Hydrofluoric Acid at 25°C.

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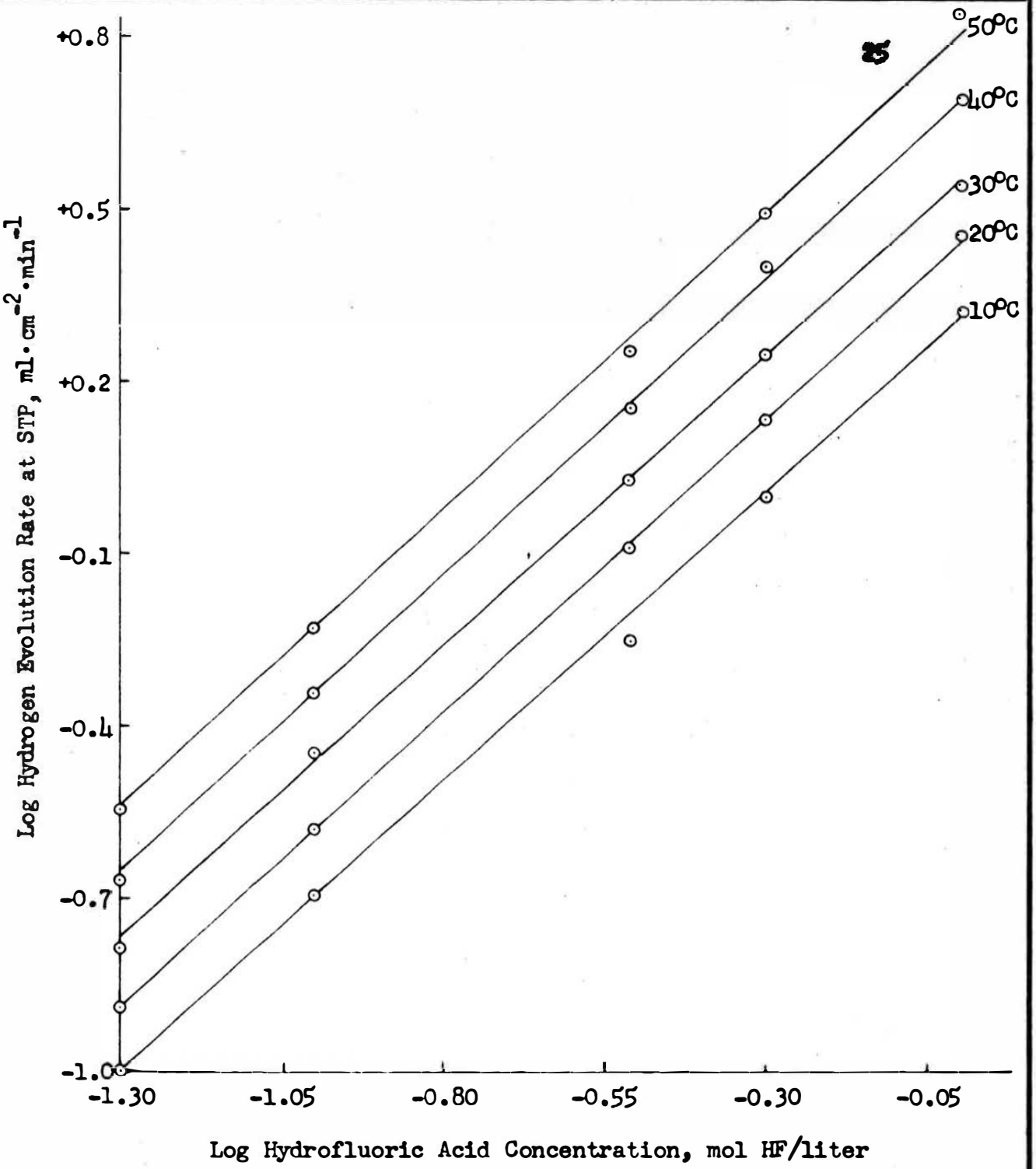

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Figure No. 8. Hydrogen Evolution Rate for the Dissolution of Hafnium in Hydrofluoric and 1.00 N Hydrochloric Acid Mixture.

SCALE:	DATE	CASE NO:
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CHECKED BY:		FIGURE NO:
APPROVED BY:		SHEET NO:

P = absolute pressure of the hydrogen

= average barometer reading during the run - vapor pressure of water - temperature correction of the barometer reading

= 735.7 - 34.1 - 3.7 = 697.9 mm Hg

T = absolute temperature of the hydrogen

= 273.2 + average thermometer reading during the run

= 273.2 + 31.2 = 304.4°K

dV = increase in volume of gases in system over the indicated time interval dt at the temperature and pressure at the gas burette

= present burette reading - previous burette reading

dV STP = increase in volume of gases in system over the indicated time interval at standard temperature and pressure

$$= dV \times \frac{273.2}{304.4} \times \frac{697.9}{760} = 0.824\ dV$$

The calculated values of dV and dV STP may be seen in the third and fourth columns of the table from which the data were taken. The values indicated with an asterisk were used to calculate the average maximum hydrogen evolution rate (dV/dt) as follows:

$$dV/dt = (1/i)(1/dt)\sum_{1}^{i}(dV\ STP) = (1/9)(1/10)(0.989 + \ldots + 1.071)$$

$$= 0.106\ ml \cdot cm^{-2} \cdot min^{-1}$$

This calculated average maximum hydrogen evolution rate is referred to in this study simply as the hydrogen evolution rate for this particular temperature and HF concentration.

P = absolute pressure of the hydrogen

= average barometer reading during the run - vapor pressure of water - temperature correction of the barometer reading

= 735.7 - 34.1 - 3.7 = 697.9 mm Hg

T = absolute temperature of the hydrogen

= 273.2 + average thermometer reading during the run

= 273.2 + 31.2 = 304.4°K

dV = increase in volume of gases in system over the indicated time interval dt at the temperature and pressure at the gas burette

= present burette reading - previous burette reading

dV STP = increase in volume of gases in system over the indicated time interval at standard temperature and pressure

$$= dV \times \frac{273.2}{304.4} \times \frac{697.9}{760} = 0.824\ dV$$

The calculated values of dV and dV STP may be seen in the third and fourth columns of the table from which the data were taken. The values indicated with an asterisk were used to calculate the average maximum hydrogen evolution rate (dV/dt) as follows:

$$dV/dt = (1/i)(1/dt)\sum_{1}^{i}(dV\ STP) = (1/9)(1/10)(0.989 + \ldots + 1.071)$$

$$= 0.106\ ml \cdot cm^{-2} \cdot min^{-1}$$

This calculated average maximum hydrogen evolution rate is referred to in this study simply as the hydrogen evolution rate for this particular temperature and HF concentration.

Effect of Temperature on the Dissolution Rate of Hafnium in Hydrofluoric Acid and Hydrofluoric-1.00 N Hydrochloric Acid Mixture

Apparatus. The apparatus used was the same as that for the measurement of the dissolution rate of hafnium in hydrofluoric acid. A diagram of the apparatus is shown in Figure 1, page 10.

Procedure. The procedure was the same as that given for the dissolution rate of hafnium in hydrofluoric acid and is located in Appendix C, pages 107 to 110.

Data and Results. The data are presented in Appendix D, pages 153 to 156.

The actual experimentation in this section included only the effect of temperature on the rate of dissolution of hafnium in hydrofluoric acid alone. The calculated values of the reaction rate constant k as affected by temperature are shown in Table VII, page 28. The effect of temperature on the rate in hydrofluoric-1.00 N hydrochloric acid mixtures was shown in the previous section (see Figure 8, page 25) and values of $\log k$ were obtained from this figure for use in this section. Data from Table VII and Figure 8 are shown in Tables VIII and IX, pages 29 and 30 and were used to make Arrhenius plots ($\log k$ versus $1/T$) for the dissolution of hafnium in hydrofluoric acid and hydrofluoric-1.00 N hydrochloric acid mixture. These plots are shown in Figure 9, page 31. The slopes of the straight lines and the resulting activation energies were calculated. The activation energy for the dissolution in hydrofluoric

TABLE VII

Reaction Rate Constants for the Dissolution of Hf Metal in Hydrofluoric Acid.

HF Conc. mol HF / liter	Reaction Rate Constant, k (ml/min of H at STP)(l. soln/mol HF)				
	5°C	15°C	25°C	35°C	45°C
0.050 -1.301*			1.94 +0.288*		
0.100 -1.000*	1.06 +0.025*	1.47 +0.167*	2.13 +0.328*	2.74 +0.438*	3.64 +0.561*
0.500 -0.301*			2.20 +0.342*		

* Logarithm of the adjacent number.

TABLE VIII

Data Used to Make Arrhenius Plot

for the Dissolution of Hf Metal in Hydrofluoric Acid.

Temperature		$(1/T) \times 10^3$	Log k
°C	°K	$°K^{-1}$	$\frac{ml}{min} \cdot \frac{l}{mol}$
5	278.2	3.595	0.025
15	288.2	3.470	0.167
25	298.2	3.353	0.328
35	308.2	3.245	0.438
45	318.2	3.143	0.561

TABLE IX

Data Used to Make Arrhenius Plot for the Dissolution of Hf Metal in HF-HCl Acid Mixture.

Temperature		$(1/T) \times 10^3$	Log k*
^oC	^oK	$^oK^{-1}$	
10	283.2	3.531	0.306
20	293.2	3.411	0.447
30	303.2	3.298	0.565
40	313.2	3.193	0.700
50	323.2	3.094	0.810

* Value from Figure No. 5.

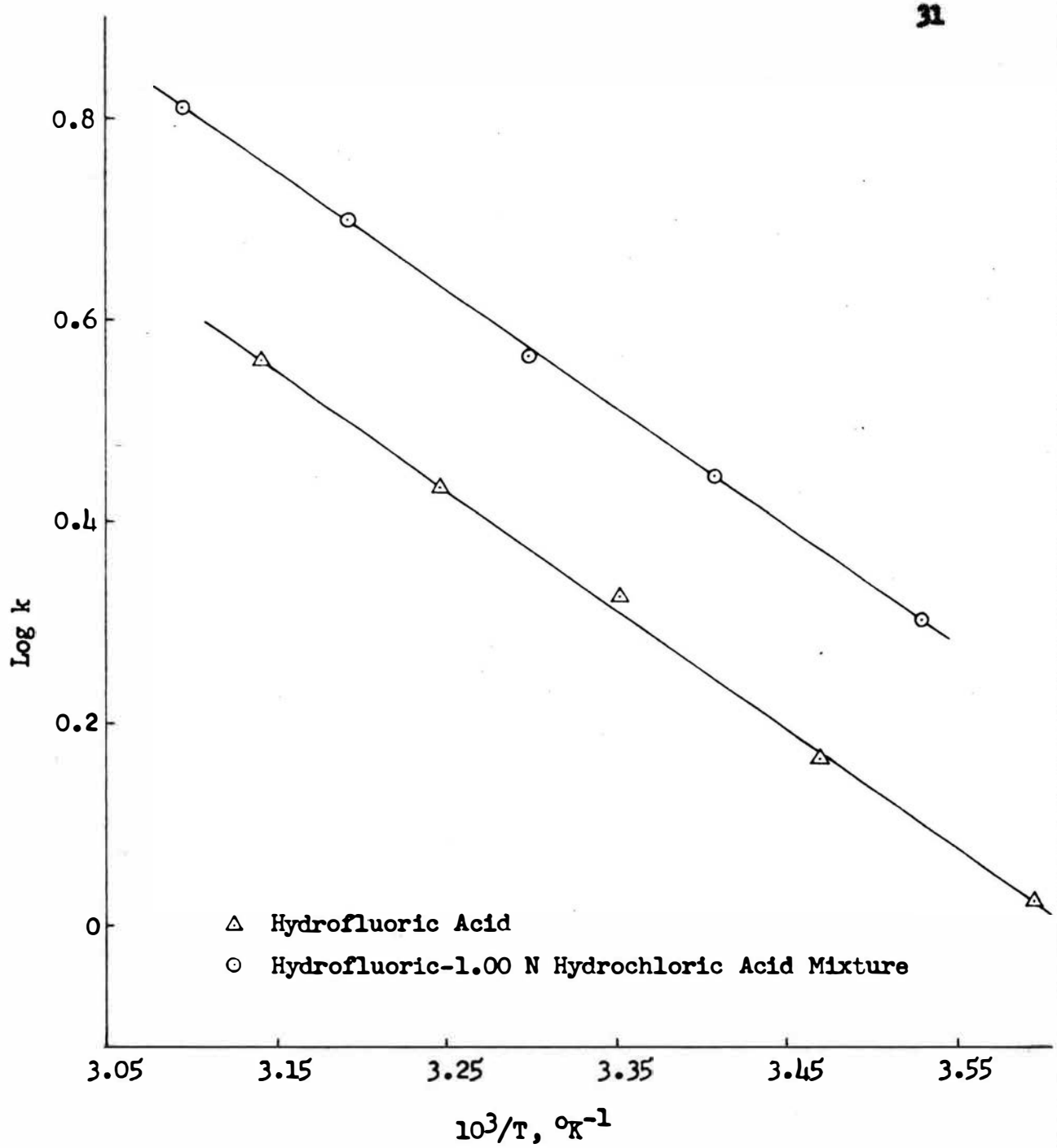

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Figure No. 9. Arrhenius Plots for the Dissolution of Hafnium in Hydrofluoric Acid and Hydrofluoric-1.00 N Hydrochloric Acid Mixture.

SCALE:	DATE	CASE NO:
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CHECKED BY:		FIGURE NO:
APPROVED BY:		SHEET NO:

acid was found to be 5.4 kcal/mol. It was 5.3 kcal/mol for the dissolution in hydrofluoric-1.00 N hydrochloric acid mixture. These values may be considered to be equal within limits of experimental error.

Sample Calculations.

1. Calculation of the reaction rate constant. The data used in this calculation were taken from Table V, page 22.

$$dV/dt = k\,(HF)^n \qquad \text{(Equation 4, page 21)}$$

But, n = 1, since the reaction was found to be first order, see page 21. Therefore,

$$k = (dV/dt)/(HF) = 0.106/0.100 = 1.06$$

2. Calculation of the activation energy. The data for this calculation were taken from Figure 9, page 31.

$$\log k = (-E_a/RT) \log e + \log A \qquad \text{(Arrhenius equation)}$$

The calculated slope from Figure 9 for the dissolution in hydrofluoric acid was equal to -1190. Thus,

$$-0.434\ E_a/R = -1190$$

$$E_a = 5{,}400 \text{ cal/mol} = 5.4 \text{ kcal/mol}$$

Effect of Various Additives on the Dissolution Rate of Hafnium in Hydrofluoric Acid

Apparatus. The apparatus was the same as that for the measurement of the dissolution rate of hafnium in hydrofluoric acid. A diagram of the apparatus is shown in Figure 1, page 10.

Procedure. The procedure for this study is divided into two parts: (1) sodium fluoride, potassium fluoride, ammonium fluoride, and lithium sulfate additions; and (2) noble metal salt, oxidizing agent, mineral acid, and various salt additions.

The detailed procedures are located in Appendix C, pages 110 to 112.

Data and Results. The data from this part of the experimentation are located in Appendix D, pages 157 to 192.

1. Fluoride Salt Additions. The results of the additions of sodium fluoride, potassium fluoride, ammonium fluoride, and lithium sulfate are shown in Figure 10. In the cases of sodium fluoride, potassium fluoride, and ammonium fluoride, a thin salt film was observed on the hafnium sample surface at the higher concentrations where passivation occurred. These salt films dissolved rapidly when the passivated sample was placed in fresh hydrofluoric acid and the reaction continued at or near its original rate. Some of the sodium salt film was removed and an analysis made by x-ray diffraction. The three major d-spacings from this salt were nearly identical with those from Na_3ZrF_7 made in a previous study. Since one would expect the hafnium salts to be isomorphous with those of zirconium, the salt film in question was very probably Na_3HfF_7. The salt films from the potassium and ammonium fluoride additions were so thin and adhered so tightly that sufficient amounts could not be removed for x-ray studies. Salt films were not observed from the lithium sulfate

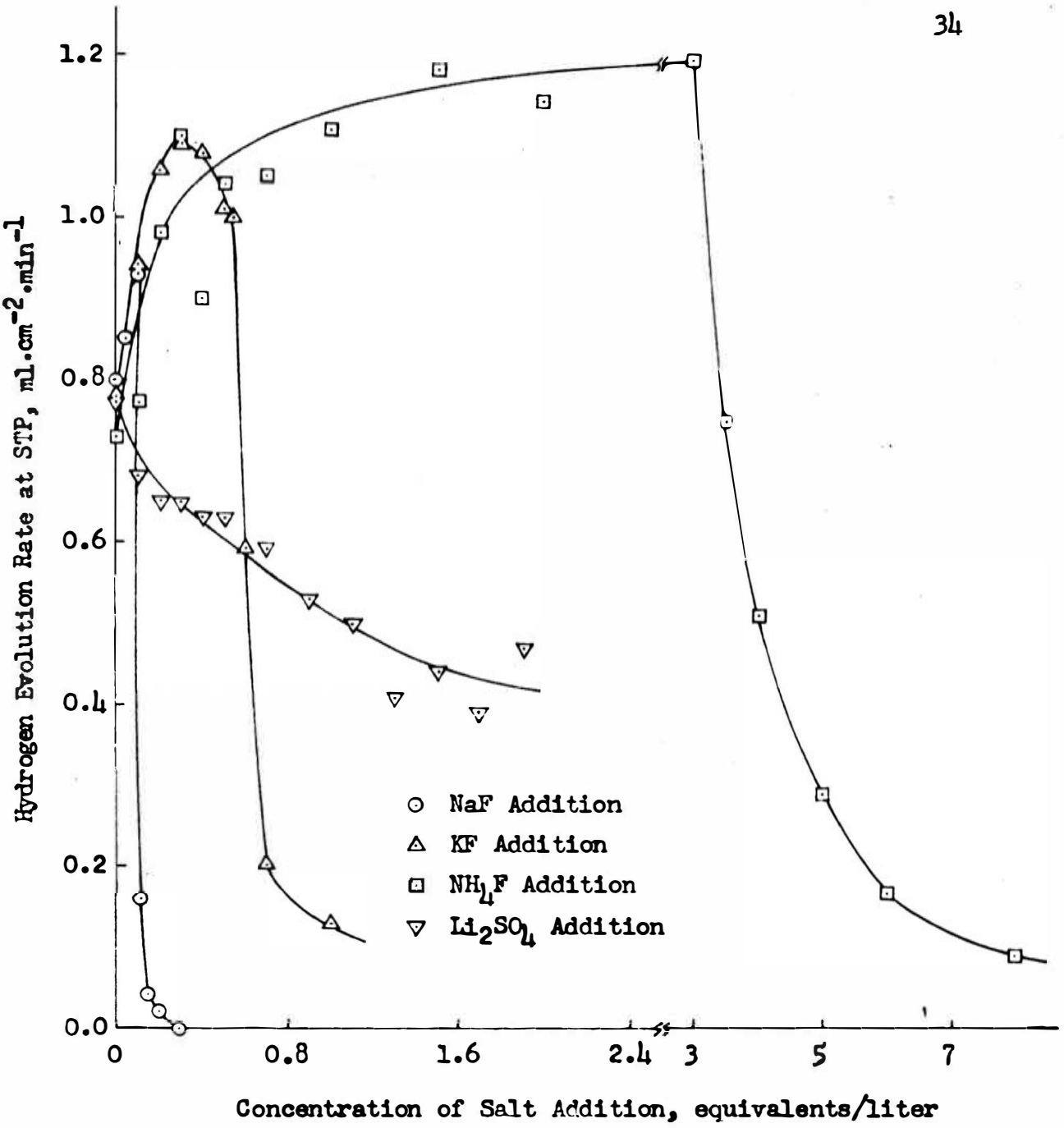

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Figure No. 10. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric Acid at 30°C with Various Fluoride Salt Additions.

SCALE:	DATE	CASE NO:
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APPROVED BY:		SHEET NO:

additions, but a precipitate identified as lithium fluoride by x-ray diffraction was found in the flask after the reaction.

2. Noble Metal Additions. The results of the additions of gold chloride, platinum chloride, and silver nitrate are shown in Figure 11. The effectiveness of passivation decreased in the order --platinum, silver, gold. Loose deposits were found on the hafnium surface and in the reaction flask after each addition. These deposits were identified by x-ray diffraction to be the reconstituted noble metals. In each case, the passivated metal surface was very shiny. The shiny surface rapidly tarnished when placed in fresh hydrofluoric acid and the reaction continued at approximately the original rate. A platinum chloride addition was also made in a hydrofluoric-1.00 N hydrochloric acid mixture. The results are shown in Figure 12, page 37. The effect of the same addition in hydrofluoric acid alone is also shown so that a comparison can be made. The addition had no apparent effect on the rate in the acid mixture, and no reconstituted metal was found in the reactor after the reaction. A very shiny surface was noted on the metal, but the underlying grain structure was still visible. The shiny films resulting from the additions in hydrofluoric acid alone had made the underlying grain structure completely invisible. This indicated that these films may have been much thicker than the one from the addition in the acid mixture.

3. Oxidizing Agent Additions. The results of the additions of sodium bismuthate, potassium permanganate, and sodium dichromate are shown in Figure 13, page 38. All the additions decreased the

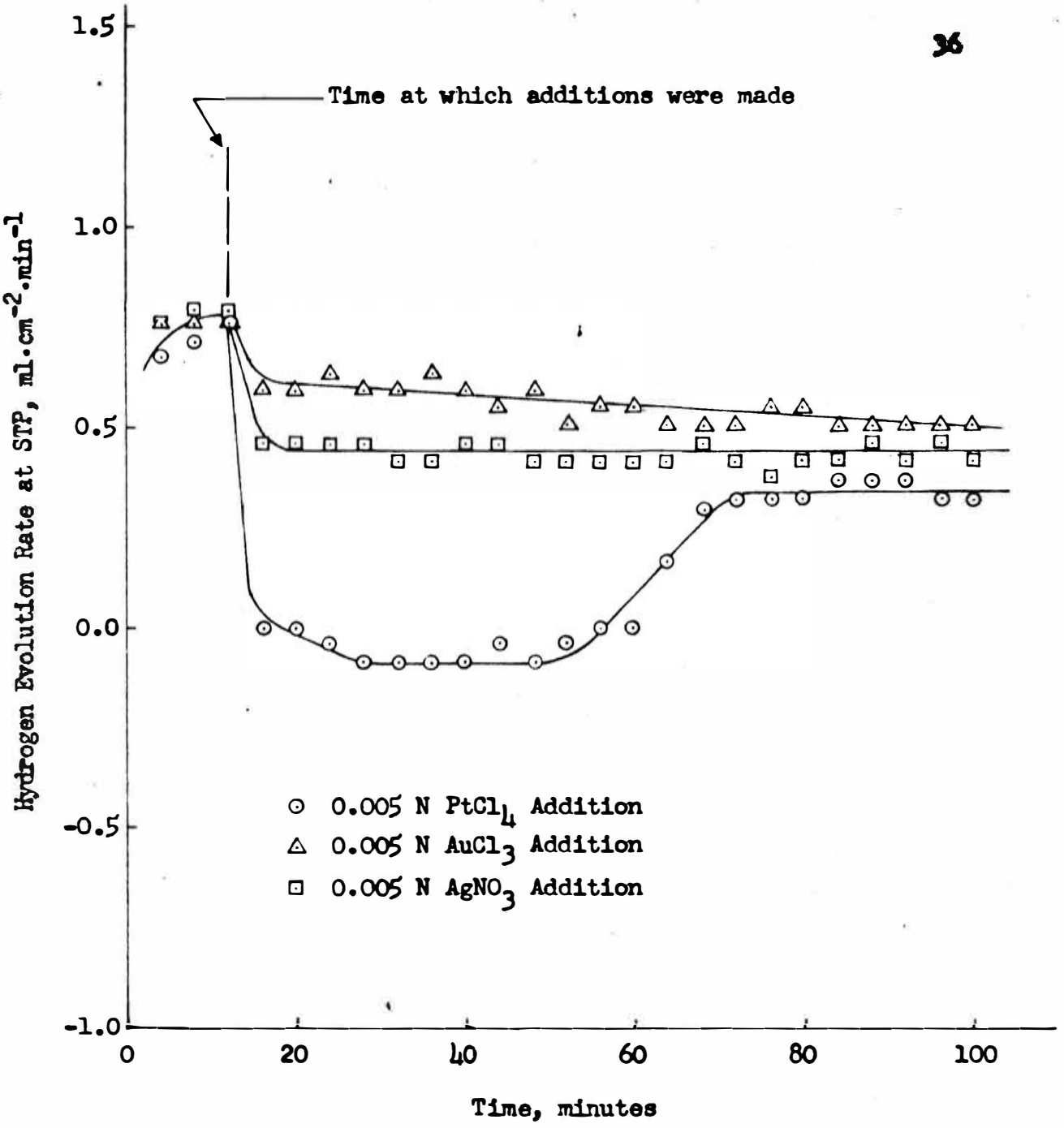

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Figure No. 11. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric Acid at 30°C with Noble Metal Salt Additions.

SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
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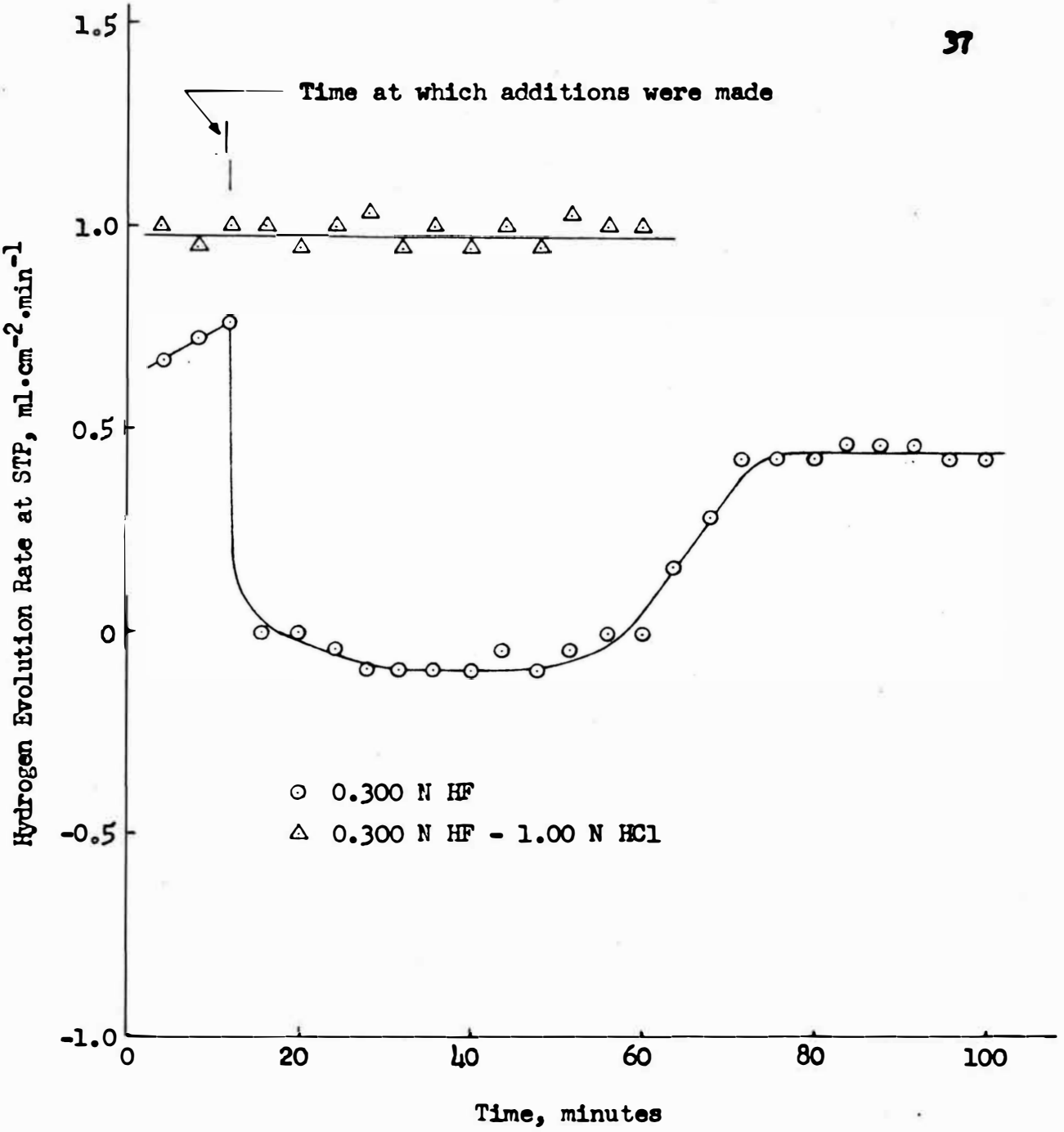

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Figure No. 12. Hydrogen Evolution Rate for the Dissolution of Hafnium at 30°C with Platinum Chloride Addition.

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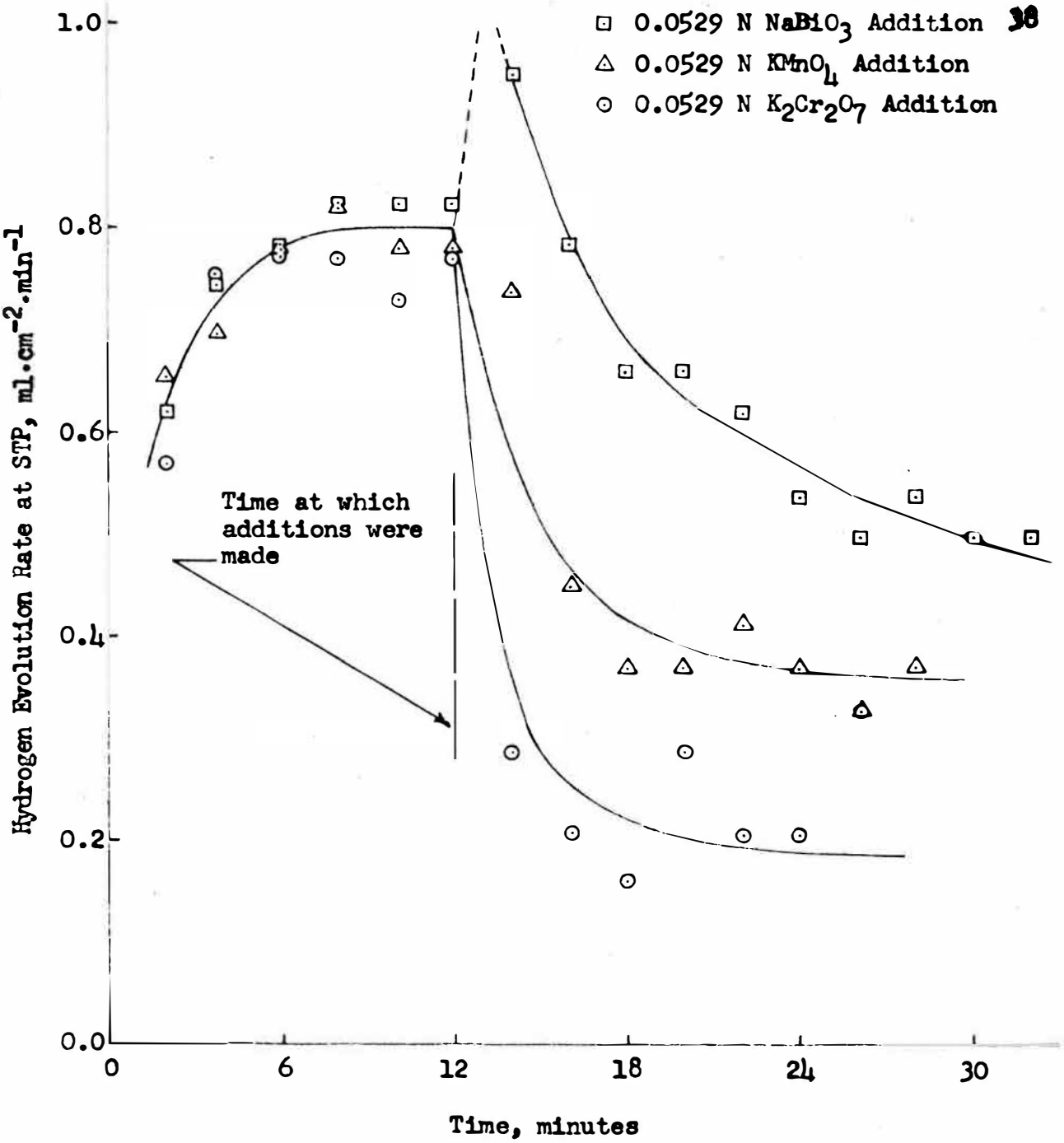

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Figure No. 13. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric Acid at 30°C with Oxidizing Agent Additions.

SCALE:	DATE	CASE	NO:
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CHECKED BY:		FIGURE	NO:
APPROVED BY:		SHEET	NO:

rate of hydrogen evolution. A reddish-brown precipitate was noted from the bismuthate addition. An x-ray analysis was performed but no identification could be made from the observed d-spacings. A shiny surface present on all the passivated samples disappeared when placed in fresh hydrofluoric acid.

4. Mineral Acid Additions. The results of the additions of hydrochloric acid, sulfuric acid, and phosphoric acid are shown in Figure 14. No large effect was caused by any of the additions. The hydrochloric acid appeared to cause a slight increase in the rate. No effect was noted for the sulfuric acid addition, and the phosphoric acid seemed to slow the reaction somewhat. Further studies were made in hydrofluoric-hydrochloric and hydrofluoric-sulfuric acid mixtures. The hydrofluoric acid concentration was held constant and the hydrochloric and sulfuric acid concentrations were varied. The results of these studies are shown in Figure 15, page 41. This shows that increasing the hydrochloric acid concentration up to 6 N appreciably increased the dissolution rate. Increasing the sulfuric acid concentration up to 8 N affected the rate only slightly.

5. Miscellaneous Salt Additions. The results of the addition of small amounts of potassium iodide, sodium chloride, potassium chloride, sodium bromide, sodium nitrate, and sodium citrate are shown in Figure 16, page 42. These additions were made at the end of the runs in which the effect of stirrer speed on the hydrogen evolution rate was being determined, so that each rate was different. It can be seen that none of the additions had any pronounced effect on the rate.

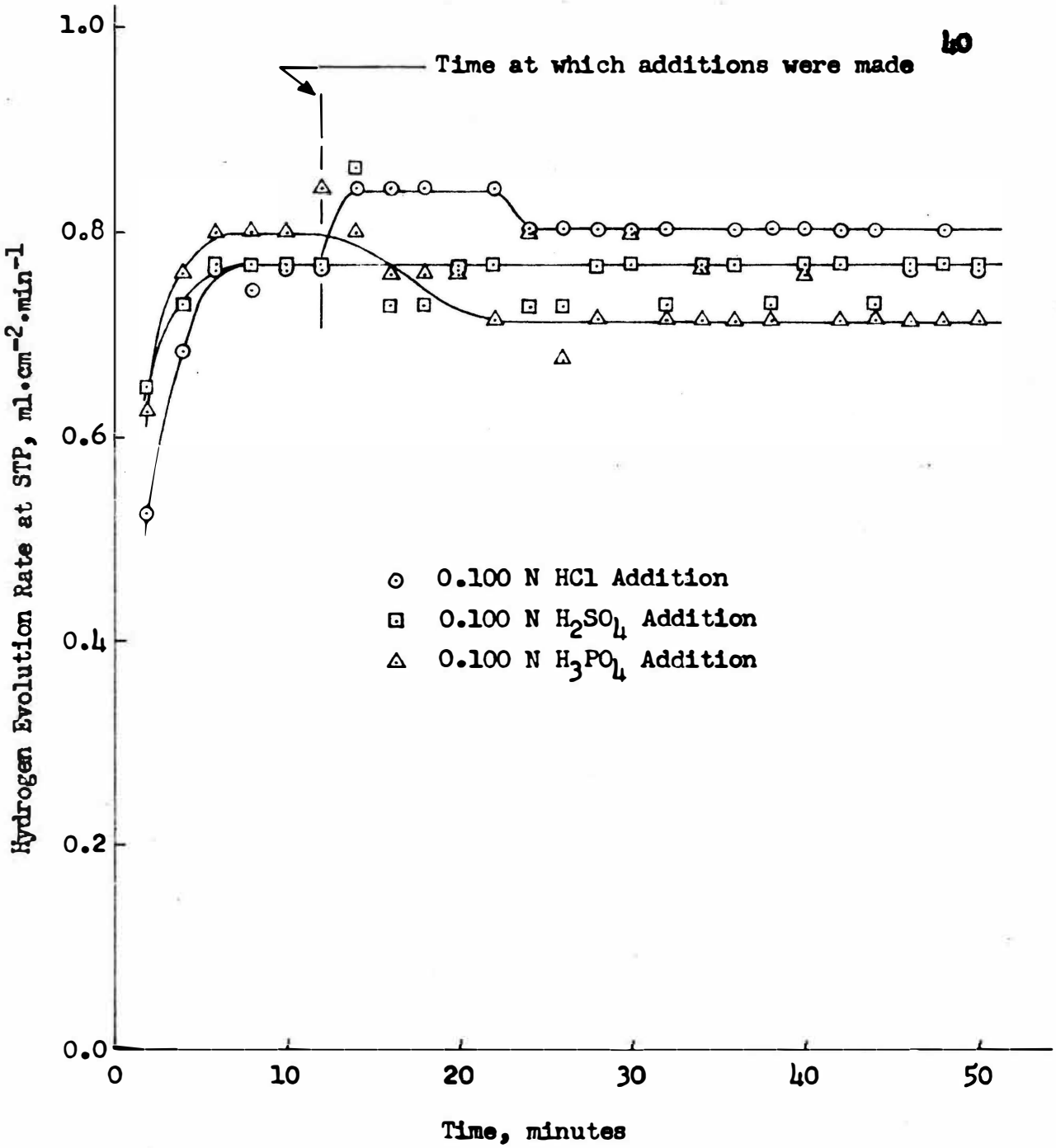

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Figure No. 14. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric Acid at 30°C with Mineral Acid Additions.

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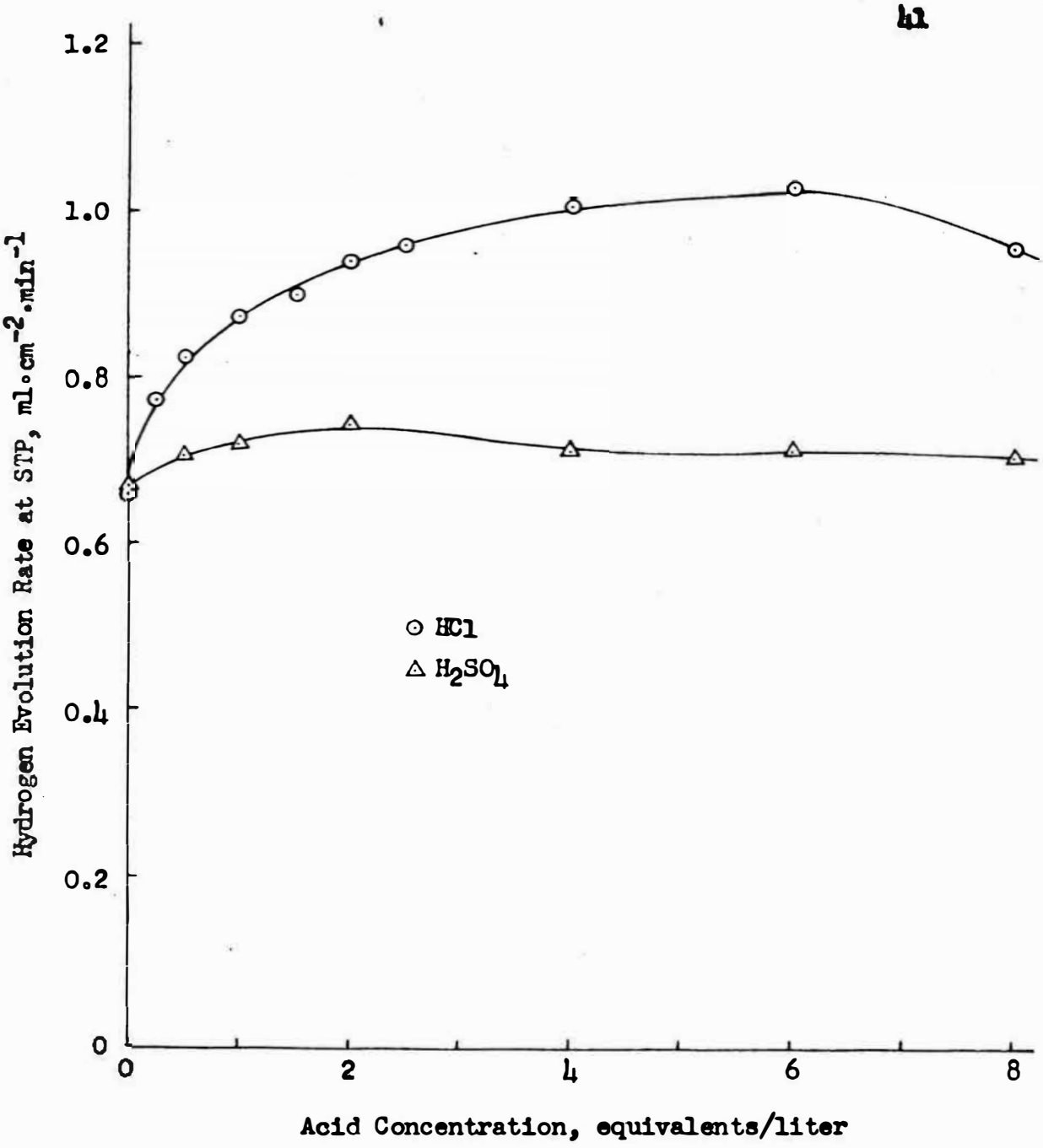

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Figure No. 15. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric - Mineral Acid Mixture at 25°C.

SCALE:	DATE	CASE NO:
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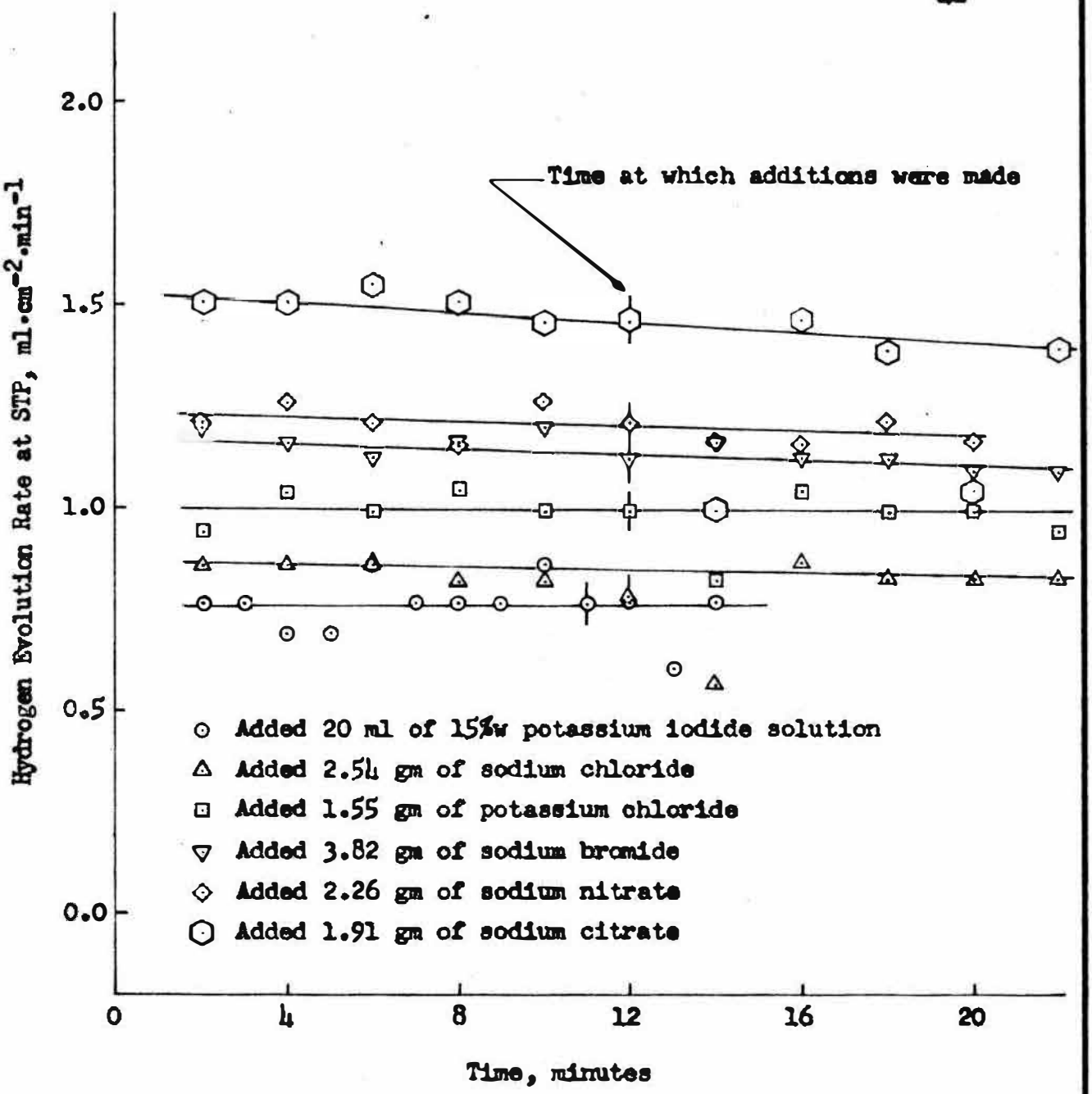

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Figure No. 16. Hydrogen Evolution Rate for the Dissolution of Hafnium in 0.300 N Hydrofluoric Acid at 30°C with Miscellaneous Salt Additions.

SCALE:	DATE	CASE	NO:
DRAWN BY:		FILE	NO:
CHECKED BY:		FIGURE	NO:
APPROVED BY:		SHEET	NO:

Sample Calculations. The sample calculations are the same as those shown on pages 21 and 26 for the dissolution rate of hafnium in hydrofluoric acid.

IV. PHASE II OF THE EXPERIMENTAL INVESTIGATION

Measurement of the Difference Effect on Hafnium in Hydrofluoric-Hydrochloric Acid Mixture

The difference effect was measured at seven different hydrofluoric acid concentrations ranging from 0.100 N to 0.700 N (all with 1.00 N hydrochloric acid) with three to seven determinations at each concentration.

Apparatus. Figure 2, page 11, shows a diagram of the apparatus used for this part of the experimentation. A description of the individual components of the apparatus is located in Appendix B, pages 101 to 105. The principle of operation of the apparatus was measurement with a gas burette of the volume increase of the gases in the system at specified time intervals with and without an anodic current flowing. The rate at which hydrogen was evolved was used to calculate the dissolution rate of the hafnium. The amount of anodic current flowing was measured directly with an ammeter and was varied by changing the resistance in the circuit.

Procedure. A detailed step-by-step procedure for this part of the experimentation is given in Appendix C, pages 112 to 116.

Data and Results. The data from these measurements are presented in Appendix D, pages 193 to 199. These tables also show the calculated values of the difference effect.

The maximum current density that could be drawn was 108.5 milliamps/cm^2 and occurred in the Hf-0.6 N HF, 1.00 N HCl-Pt cell. The results are summarized in Figure 17, page 45, in which the difference effect is shown with varying current density. The slope of a straight line fitted through the points was calculated by the method of least squares. This gave a value for the constant K equal to 10.0 for the empirical equation:

$$\Delta = K I = 10.0 I \qquad (5)$$

where,

Δ = difference effect, $mm^3 \cdot cm^{-2} \cdot min^{-1}$

I = current density, milliamps$\cdot cm^{-2}$

K = constant for hafnium in HF-1.00 N HCl acid mixture

= 10.0 ± 0.3 (for 95% confidence interval)

As a point of interest, Figures 18 and 19, pages 46 and 47, were made to show the anodic current density developed by the cells as a function of the setting on the resistance box in the ammeter circuit (approximately equal to the external resistance of the cell) and the maximum steady current density that could be obtained in the cells as a function of the hydrofluoric acid concentration.

Sample Calculations. The following illustrates the calculation of the difference effect for hafnium dissolving in 0.300 N

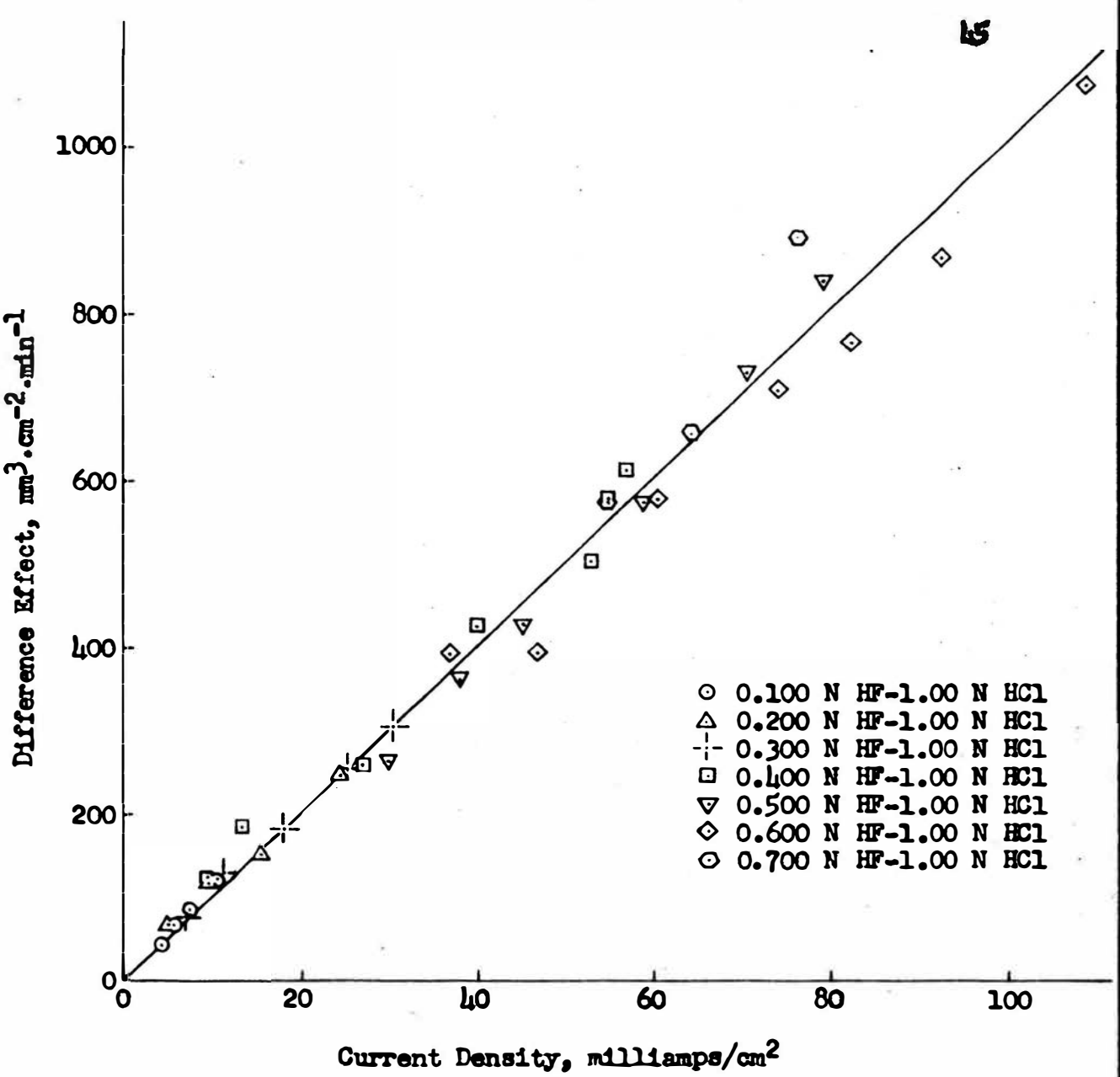

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Figure No. 17. Difference Effect on Hafnium in Hydrofluoric-Hydrochloric Acid Mixture at 25°C.

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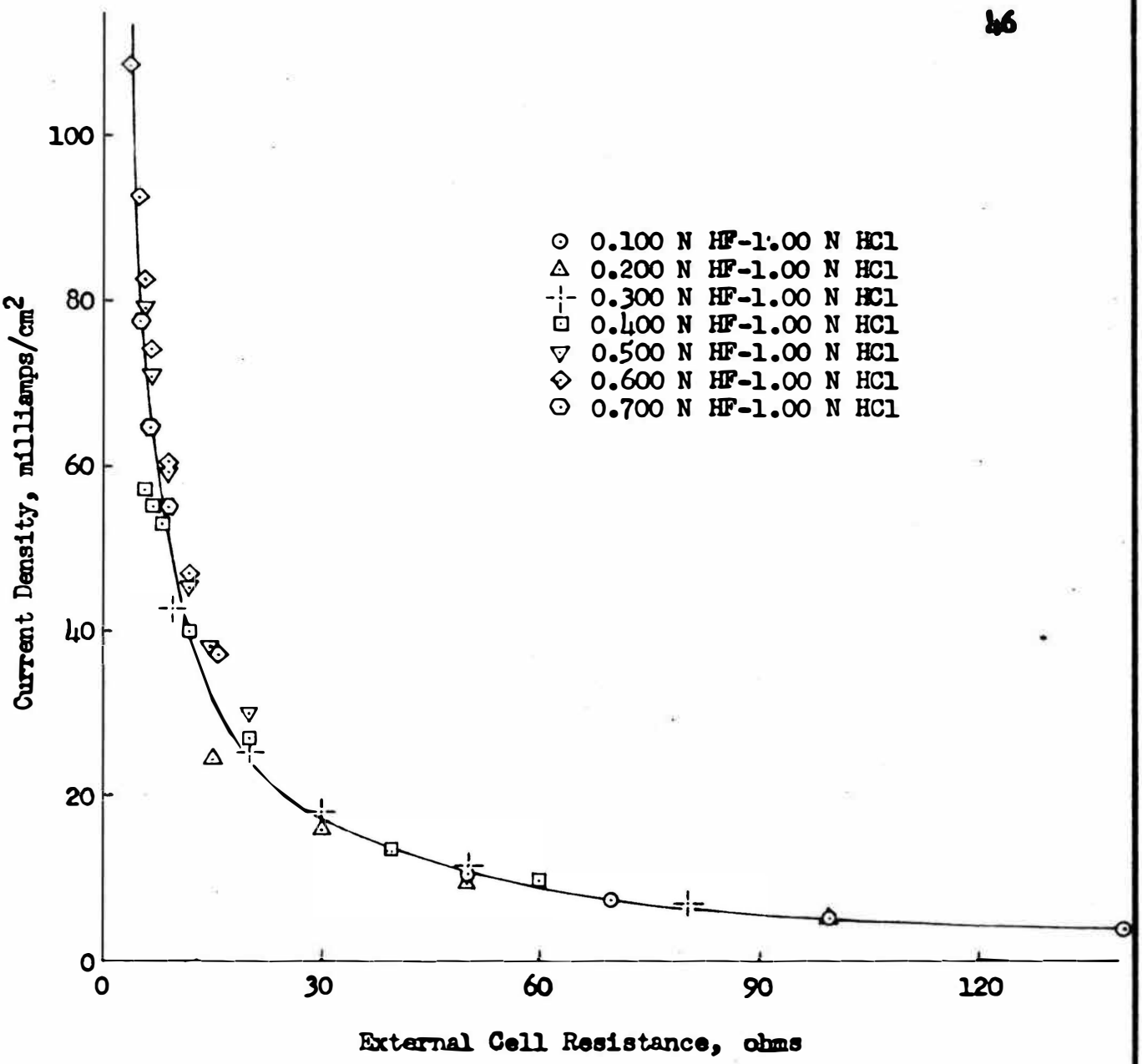

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Figure No. 18. Anodic Current Density Developed in Hf-HF, HCl-Pt Cell at 25°C during Difference Effect Measurements.

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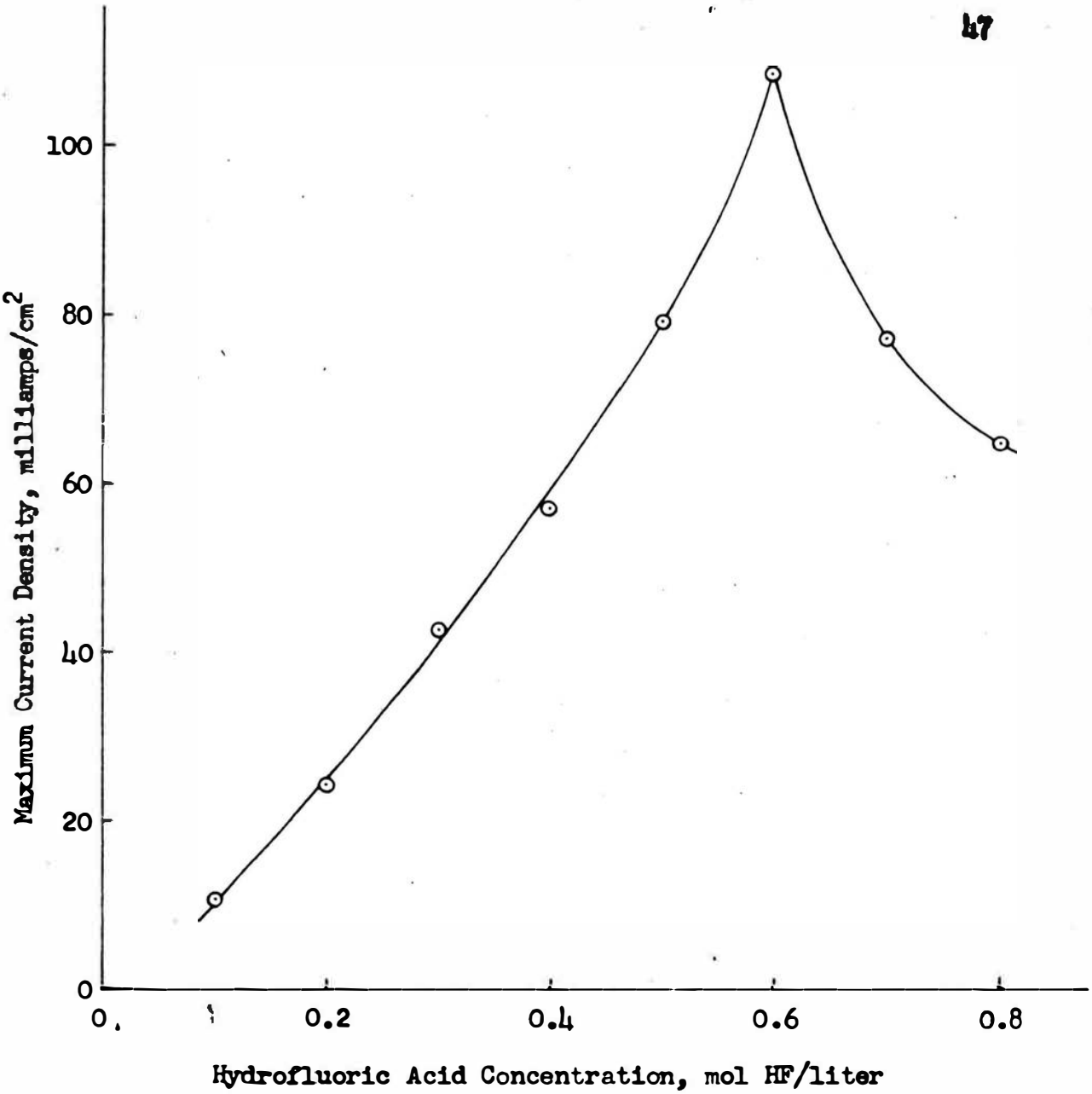

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Figure No. 19. Maximum Current Density Developed in Hf-HF, 1.00N HCl-Pt Cell at 25°C during Difference Effect Measurements.

SCALE:	DATE	CASE NO:
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CHECKED BY:		FIGURE NO:
APPROVED BY:		SHEET NO:

hydrofluoric-1.00 N hydrochloric acid mixture at 25°C. The data for these calculations are taken from Appendix D, page 195. The area of the hafnium electrode was 1.00 cm^2, so all the rates and currents can be put on a "per cm^2" basis.

P = absolute pressure of the hydrogen

= average barometer reading during the run - vapor pressure of water - temperature correction of the barometer reading

= 733.2 - 31.8 - 3.6 = 697.8 mm Hg

T = absolute temperature of the hydrogen

= 273.2 + average thermometer reading during the run

= 273.2 + 30.0 = 303.2°K

dV = increase in volume of gases in system over the indicated time interval dt at the temperature and pressure at the gas burette

= present burette reading - previous burette reading

dV STP = increase in volume of gases in system over the indicated time interval at standard temperature and pressure divided by the time interval

$$= \frac{dV}{5} \times \frac{273.2}{303.2} \times \frac{697.8}{760} = 0.1655\ dV$$

The calculated values of dV and dV STP may be seen in the third and fourth columns of the table from which the data were taken.

dV_1 = average hydrogen evolution rate from the hafnium electrode with no current flowing

= average of dV STP immediately preceding and proceeding that with current flowing

= 0.5 (596 + 645) = 620 $mm^3 \cdot cm^{-2} \cdot min^{-1}$

dV_t = average hydrogen evolution rate from both the hafnium and platinum electrodes with anodic current flowing

= 0.5 (546 + 579) = 562 $mm^3 \cdot cm^{-2} \cdot min^{-1}$

6.97 I = hydrogen liberated at platinized platinum electrode due to anodic current

= (6.97)(18.0) = 125 $mm^3 \cdot cm^{-2} \cdot min^{-1}$

Δ = difference effect

= hydrogen evolution rate from hafnium electrode without current flowing - hydrogen evolution rate from hafnium electrode with current flowing

= $dV_1 - dV_t + 6.97\ I$

= 620 - 562 + 125 = 183 $mm^3 \cdot cm^{-2} \cdot min^{-1}$

Values of the difference effect for other current densities were calculated in a similar manner and are shown in the table.

The calculations for the constant K in Equation 5, page 44, by the method of least squares are shown in Appendix E, pages 214 to 217.

V. PHASE III OF THE EXPERIMENTAL INVESTIGATION

Measurement of the Dissolution Potentials of Hafnium in Hydrofluoric Acid and Hydrofluoric-Hydrochloric Acid Mixtures

Apparatus. Figure 3, page 13, shows a diagram of the apparatus used for this part of the experimentation. A description of the individual components of the apparatus is located in Appendix B, pages 101 to 105. The principle of operation of the apparatus was measurement with a potentiometer of the potential developed by a cell consisting of a hafnium electrode dissolving in hydrofluoric acid bridged to a 1.00 N calomel electrode. Two salt bridges were used. The main (saturated potassium chloride) bridge was used to eliminate liquid junction potentials and prevent hydrofluoric acid from contacting the calomel electrode. The purpose of the auxiliary (0.1$\frac{1}{4}$ N HF) bridge was to prevent contamination of the hydrofluoric acid in the hafnium half-cell by the potassium chloride solution. This concentration of hydrofluoric acid was used in the auxiliary bridge as it was low enough not to appreciably attack glass and still possessed sufficient conductivity to provide adequate potentiometer sensitivity. The stirrer in the hafnium half-cell helped to prevent hydrogen polarization and to maintain a homogeneous temperature and concentration in the acid. The potential of the cell was measured with no current flowing in the external circuit. The potential of the hafnium electrode (on the hydrogen scale) was obtained by subtracting the potential of the reference electrode from the potential of the cell.

Procedure. A detailed step-by-step procedure for this part of the experimentation is given in Appendix C, pages 116 to 118.

Data and Results. The data from this part of the experimentation are presented in Appendix D, pages 200 to 210.

The results of the dissolution potential measurements are shown in Figures 20, 21, and 22, pages 52 to 54. Figure 20 shows the dissolution potentials for different hydrofluoric acid concentrations as a function of time. It may be noted that the potentials increased (became less noble or more reactive) as the hydrofluoric acid concentration increased, and that in general, the electrode became more noble as the reaction time increased, reaching a fairly constant value after about one hour. Figure 21 is a plot of the same data but with the hydrofluoric acid concentration as the independent variable. It very readily shows the dependence of the electrode potential on the length of the reaction time. The effect of hydrochloric acid in hydrofluoric-hydrochloric acid mixtures is shown in Figure 22. The dissolution potentials became more noble in the acid mixture, showing no other uniform trend.

Sample Calculations. The following illustrates the calculation of the dissolution potential of the hafnium electrode for a specific time and hydrofluoric acid concentration. The experimental value of the potential of the cell (potentiometer reading) is taken for an elapsed time of one minute from Appendix D, page 200.

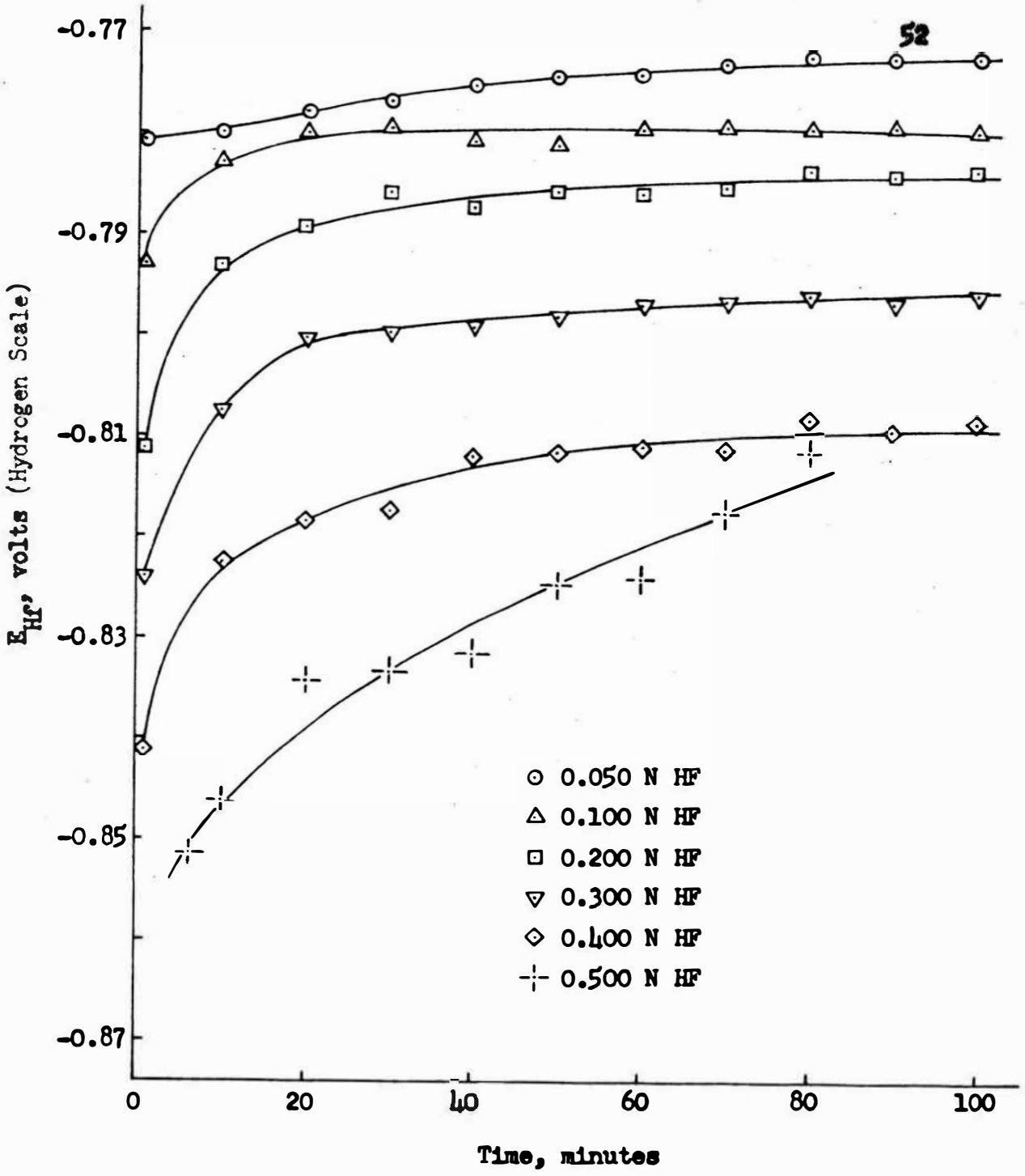

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Figure No. 20. Dissolution Potential of Hafnium Electrode in Hydrofluoric Acid at 25°C.

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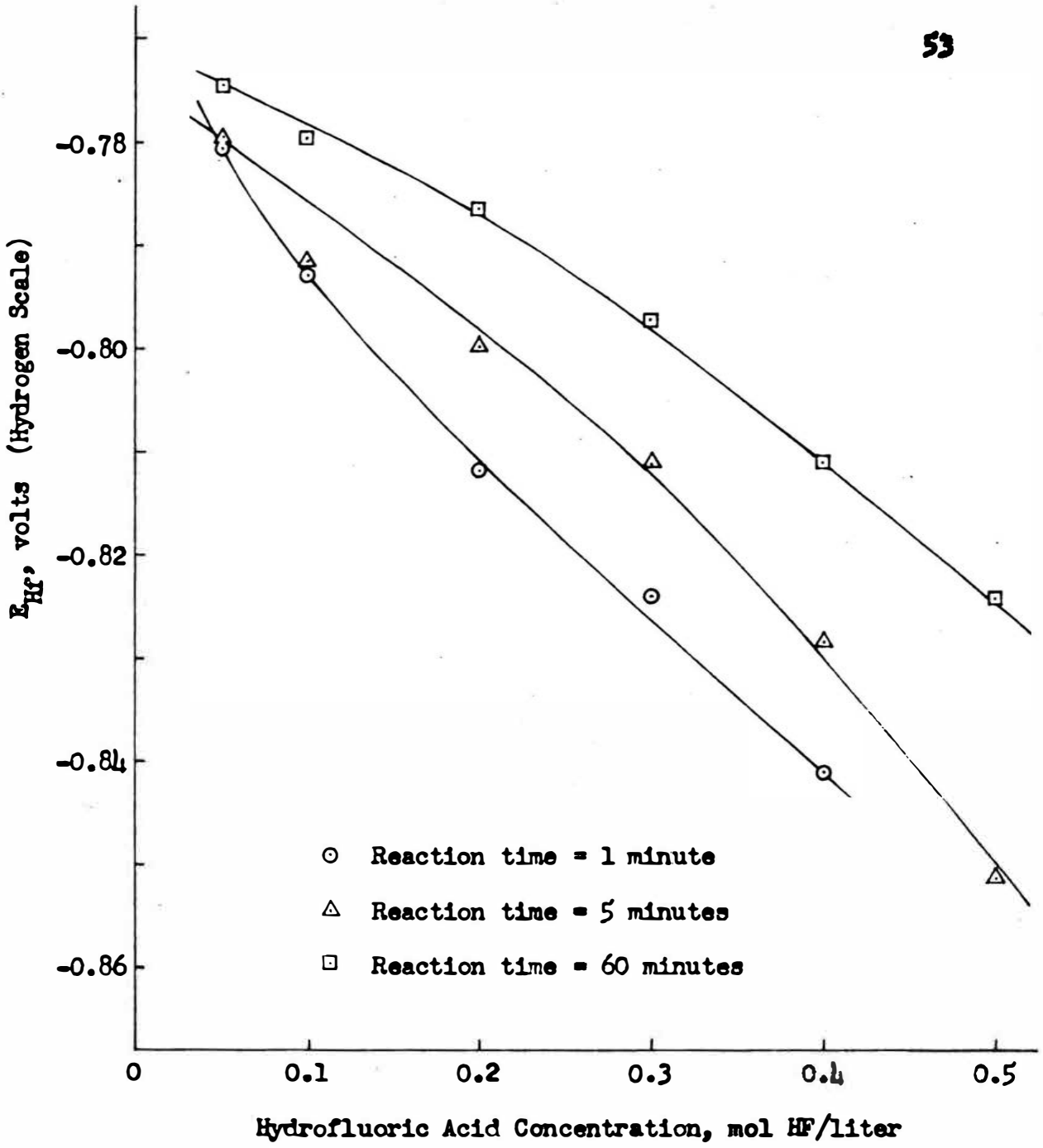

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Figure No. 21. Dissolution Potential of Hafnium Electrode in Hydrofluoric Acid at 25°C.

SCALE:	DATE	CASE NO:
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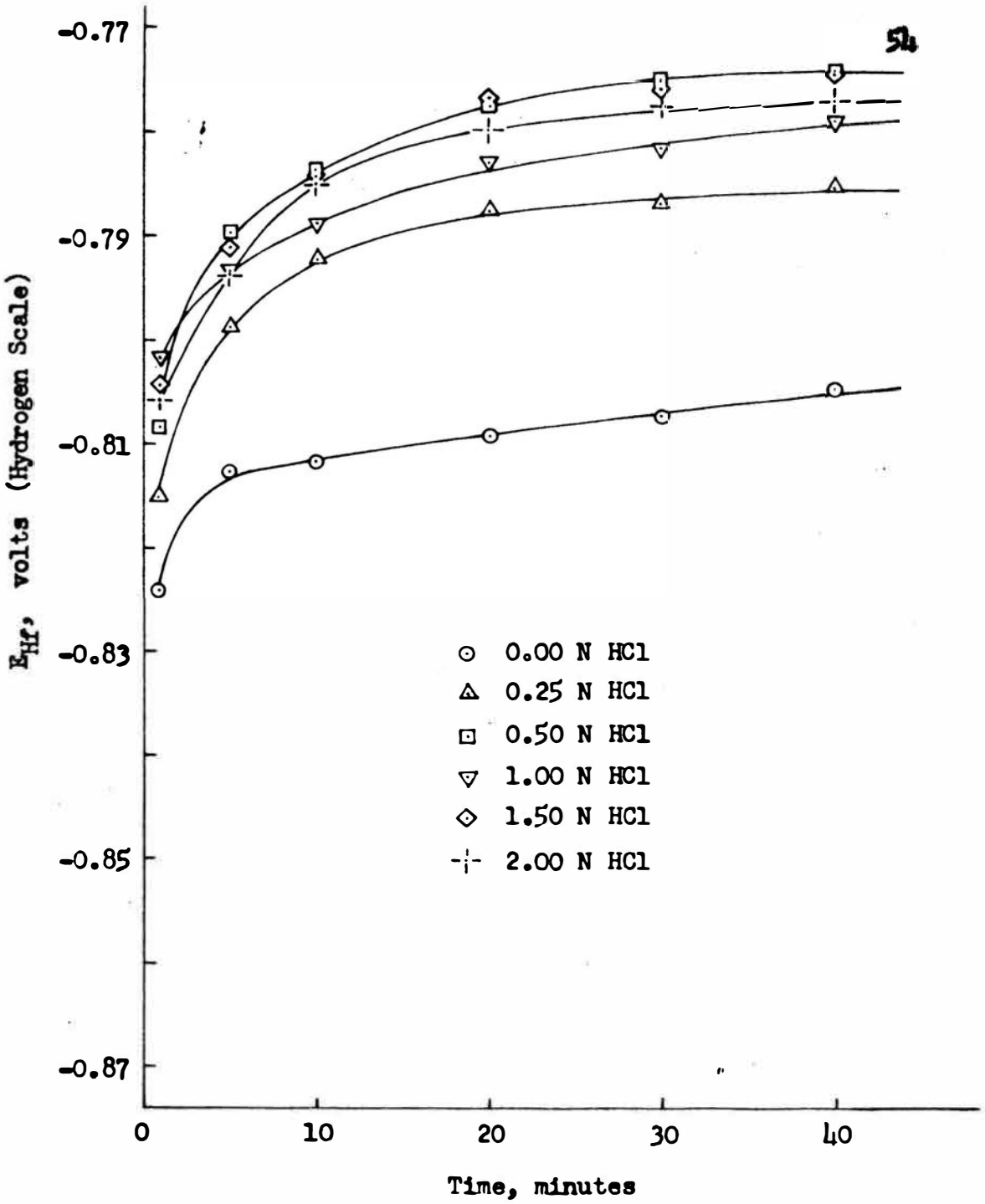

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Figure No. 22. Dissolution Potential of Hafnium Electrode in 0.300 N Hydrofluoric-Hydrochloric Acid Mixture at 25°C.

SCALE:	DATE	CASE NO:
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potentiometer reading = 1.0608 volts

potential of 1 N calomel electrode at 25°C = 0.2802 volts

dissolution potential of hafnium electrode

= 0.2802 - 1.0608 = -0.7806 volts

The remaining potentials were calculated in a similar manner.

Effect of Various Additions on the Dissolution Potentials of Hafnium in Hydrofluoric Acid

Apparatus. The apparatus was the same as that for the measurement of the dissolution potentials in hydrofluoric acid. A diagram of the apparatus is shown in Figure 3, page 13.

Procedure. The procedure for this part of the experimentation is located in Appendix C, page 119.

Data and Results. The data from this part of the experimentation are presented in Appendix D, pages 204 to 209.

1. Fluoride Salt Additions. The results of the addition of sodium fluoride, potassium fluoride, ammonium fluoride, and lithium sulfate are shown in Figure 23. Amounts of the salts were added that had previously passivated the hafnium surface in the dissolution rate studies. It can be seen that the potential became less noble in each case. Thin salt layers were noted on the surface of the hafnium electrode after the additions of sodium fluoride, potassium fluoride, and ammonium fluoride.

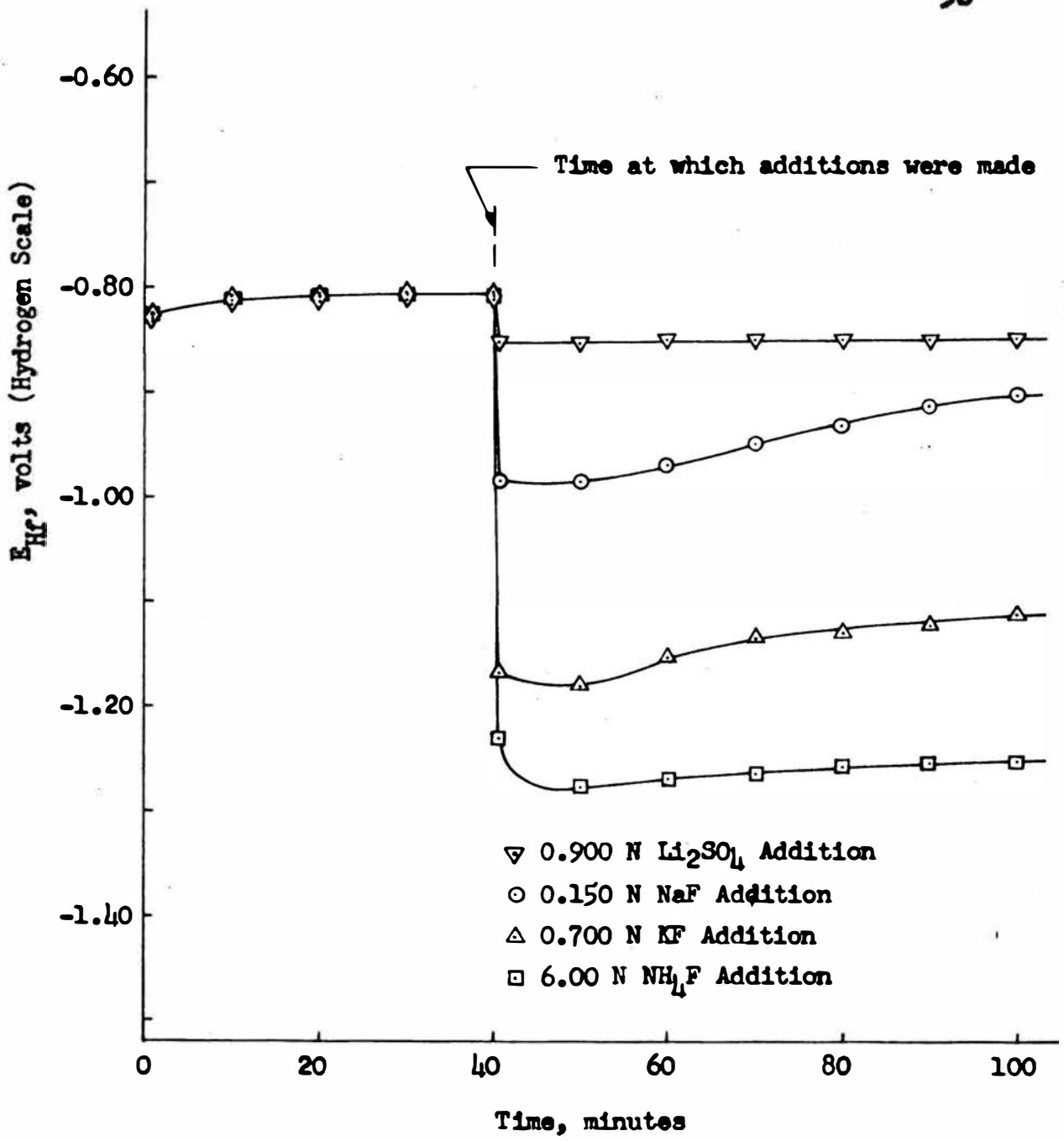

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Figure No. 23. Dissolution Potential of Hafnium Electrode in 0.300 N Hydrofluoric Acid at 25°C with Various Fluoride Salt Additions.

SCALE:	DATE	CASE	NO:
DRAWN BY:		FILE	NO:
CHECKED BY:		FIGURE	NO:
APPROVED BY:		SHEET	NO:

2. Noble Metal Additions. The results of the additions of gold chloride, platinum chloride, and silver nitrate are shown in Figure 24. Both the gold chloride and platinum chloride addition caused the potential to become more noble. The gold chloride had the most pronounced effect, and also produced a mirror-like polish on the electrode surface. The polished surface disappeared rapidly when placed in fresh hydrofluoric acid. The platinum chloride addition had an immediate pronounced effect upon the potential, but the effect gradually decreased with time. The electrode surface from this run was also shiny, but much less than from the gold chloride addition. The silver nitrate addition had no noticeable effect on the electrode. The reconstituted noble metal was found in the reaction beaker after all the additions. In the case of the silver nitrate addition, small needle-like crystals of the silver metal were found. Figure 25, page 59, shows the effect of the platinum chloride addition on the potential in hydrofluoric-1.00 N hydrochloric acid mixture. The effect of the same addition in hydrofluoric acid alone is also shown so that a comparison can be made. No reconstituted metal was found in the reaction beaker after the run.

3. Oxidizing Agent Additions. The results of the additions of sodium bismuthate, potassium permanganate, and sodium dichromate are shown in Figure 26, page 60. The potassium permanganate and potassium dichromate additions made the potentials slightly more negative. Sodium bismuthate had the opposite effect, again producing the reddish brown precipitate previously mentioned on page 39.

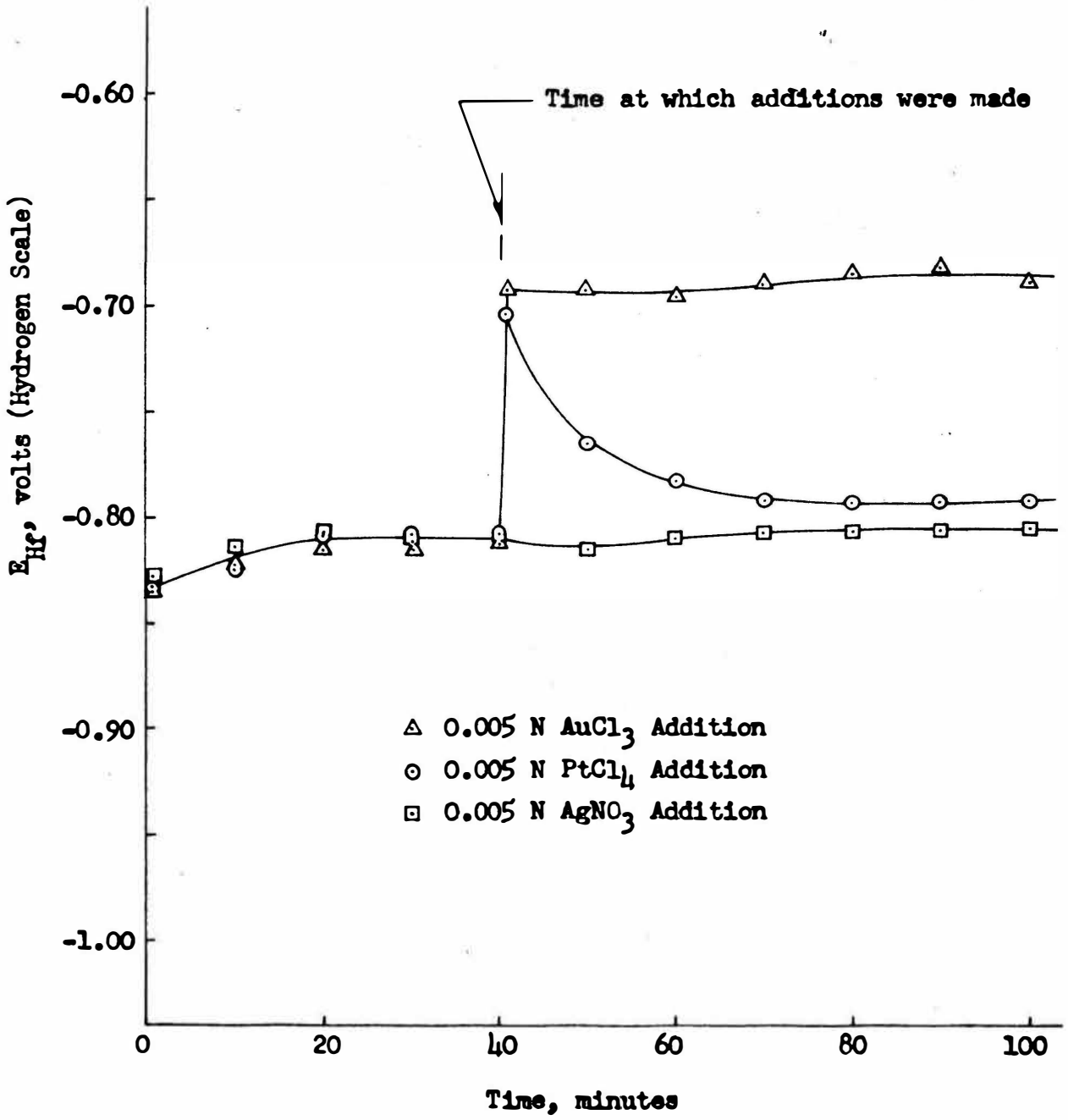

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Figure No. 24. Dissolution Potential of Hafnium Electrode in 0.300 N Hydrofluoric Acid at 25°C with Noble Metal Salt Additions.

SCALE:	DATE	CASE NO:
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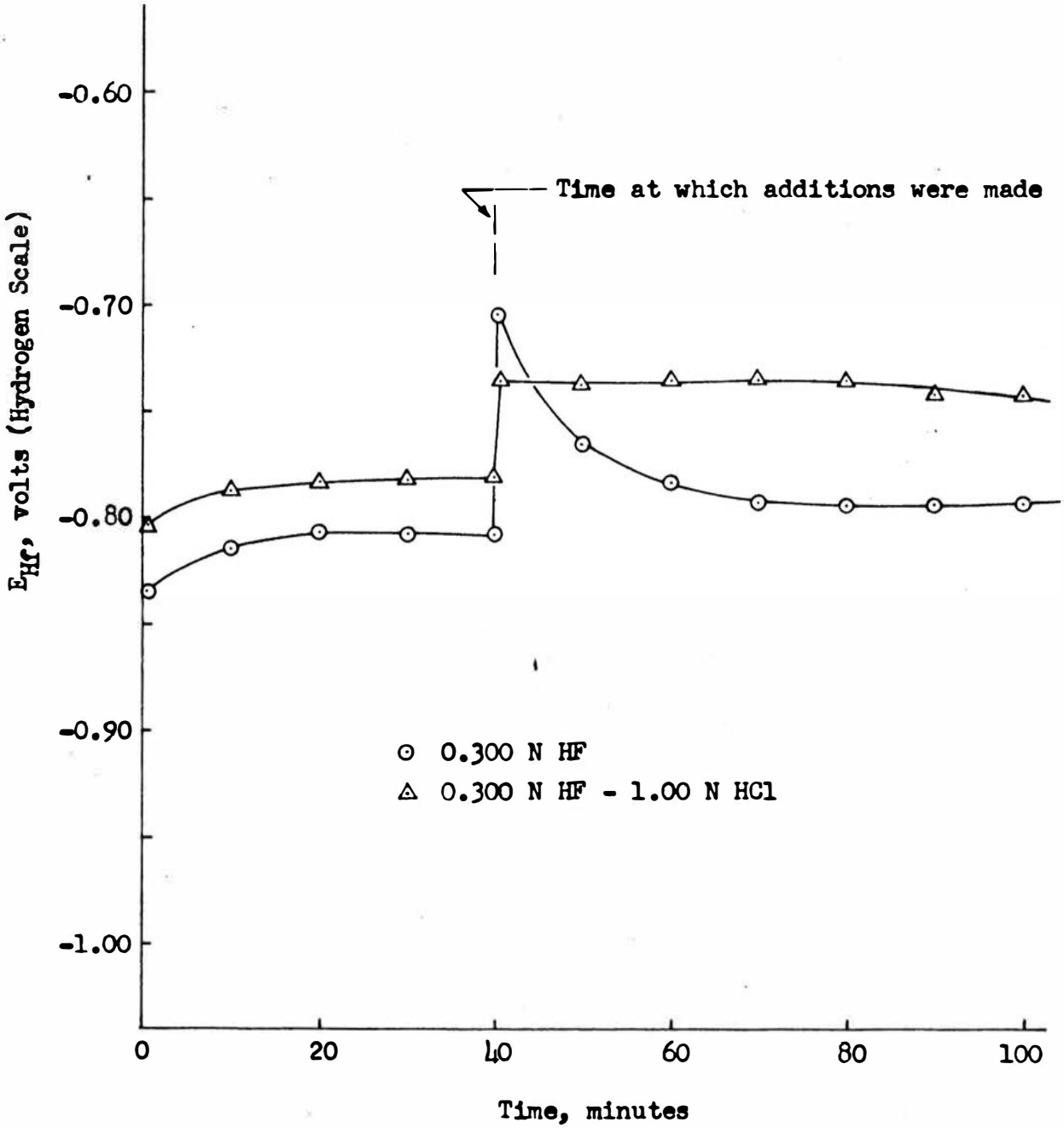

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Figure No. 25. Dissolution Potential of Hafnium Electrode at 25°C with Platinum Chloride Addition.

SCALE:	DATE	CASE NO:
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APPROVED BY:		SHEET NO:

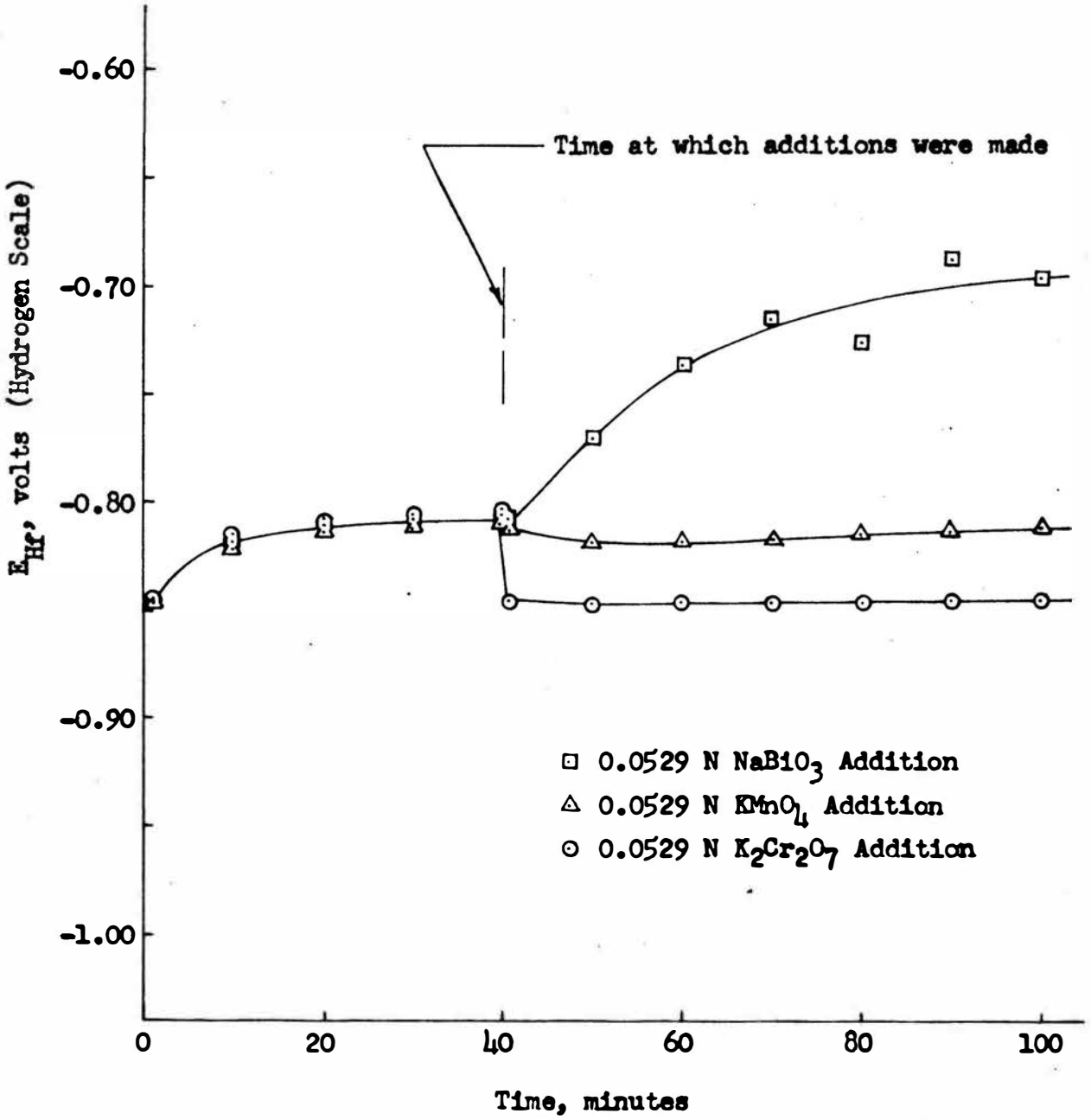

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Figure No. 26. Dissolution Potential of Hafnium Electrode in 0.300 N Hydrofluoric Acid at 25°C with Oxidizing Agent Additions.

SCALE:	DATE	CASE NO:
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4. Mineral Acid Additions. The results of the additions of hydrochloric acid, sulfuric acid, and phosphoric acid are shown in Figure 27. The sulfuric acid and phosphoric acid additions had no noticeable effect on the potential. The hydrochloric acid addition had a slightly larger effect, causing the potential to become more noble. This had been previously observed in the dissolution potentials in hydrofluoric-hydrochloric acid mixtures.

Sample Calculations. The calculations are the same as those given for the dissolution potentials on pages 51 and 55.

Effect of Current Density on the Dissolution Potentials of Hafnium in Hydrofluoric Acid

Apparatus. The apparatus was the same as that for the measurement of the dissolution potentials of the hafnium electrode (see Figure 3, page 13), except that a platinized platinum electrode was also introduced into the reaction beaker. A separate circuit containing an ammeter and a variable resistance box was used to connect the two electrodes.

Procedure. The procedure for this part of the experimentation is located in Appendix C, pages 119 and 120.

Data and Results. The data from this part of the experimentation are presented in Appendix D, page 210.

The results are shown in Figure 28, page 63, for hydrofluoric acid concentrations of 0.100, 0.200, and 0.300 N. This figure shows

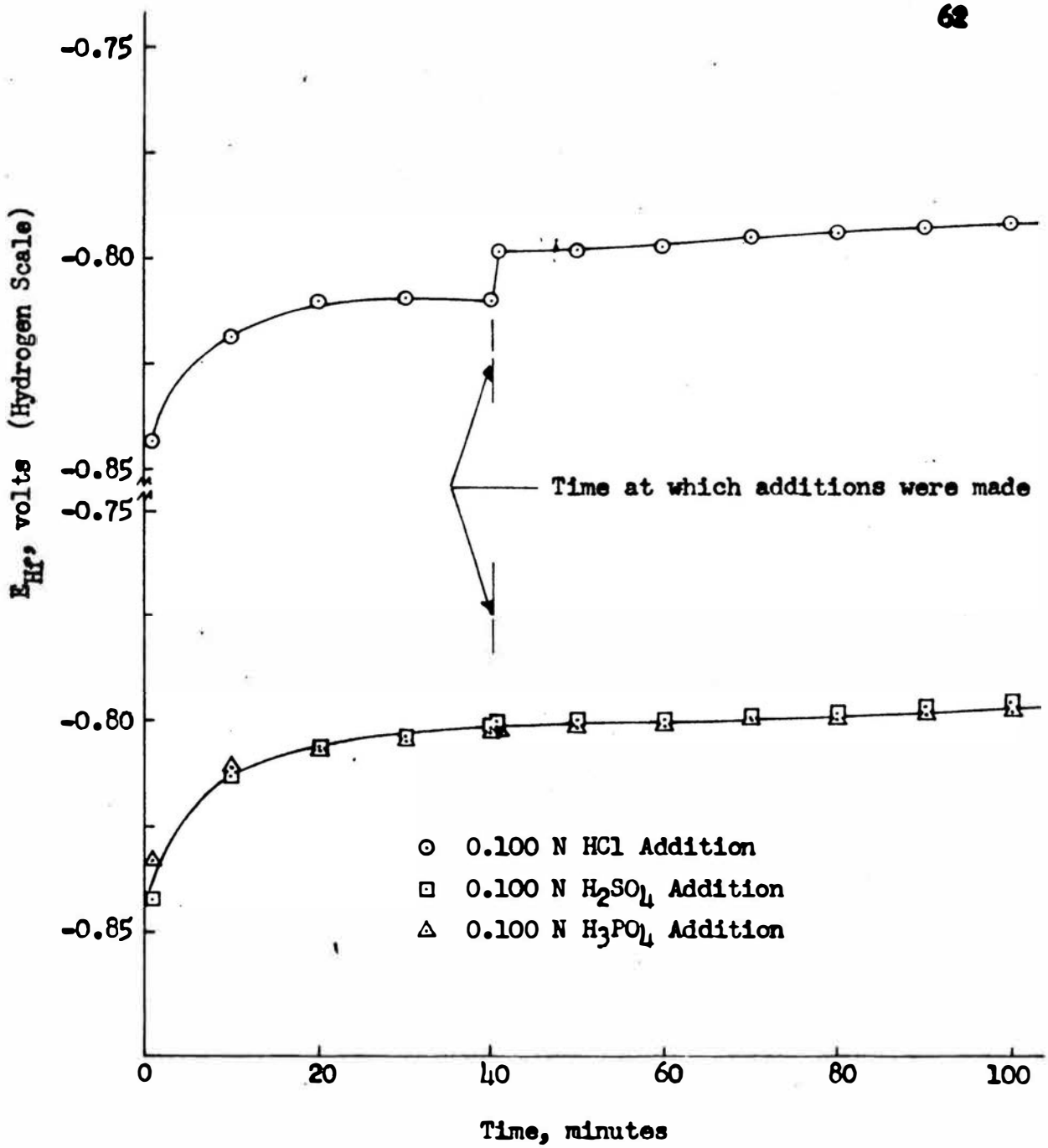

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Figure No. 27. Dissolution Potential of Hafnium Electrode in 0.300 N Hydrofluoric Acid at 25°C with Mineral Acid Additions.

SCALE:	DATE	CASE NO:
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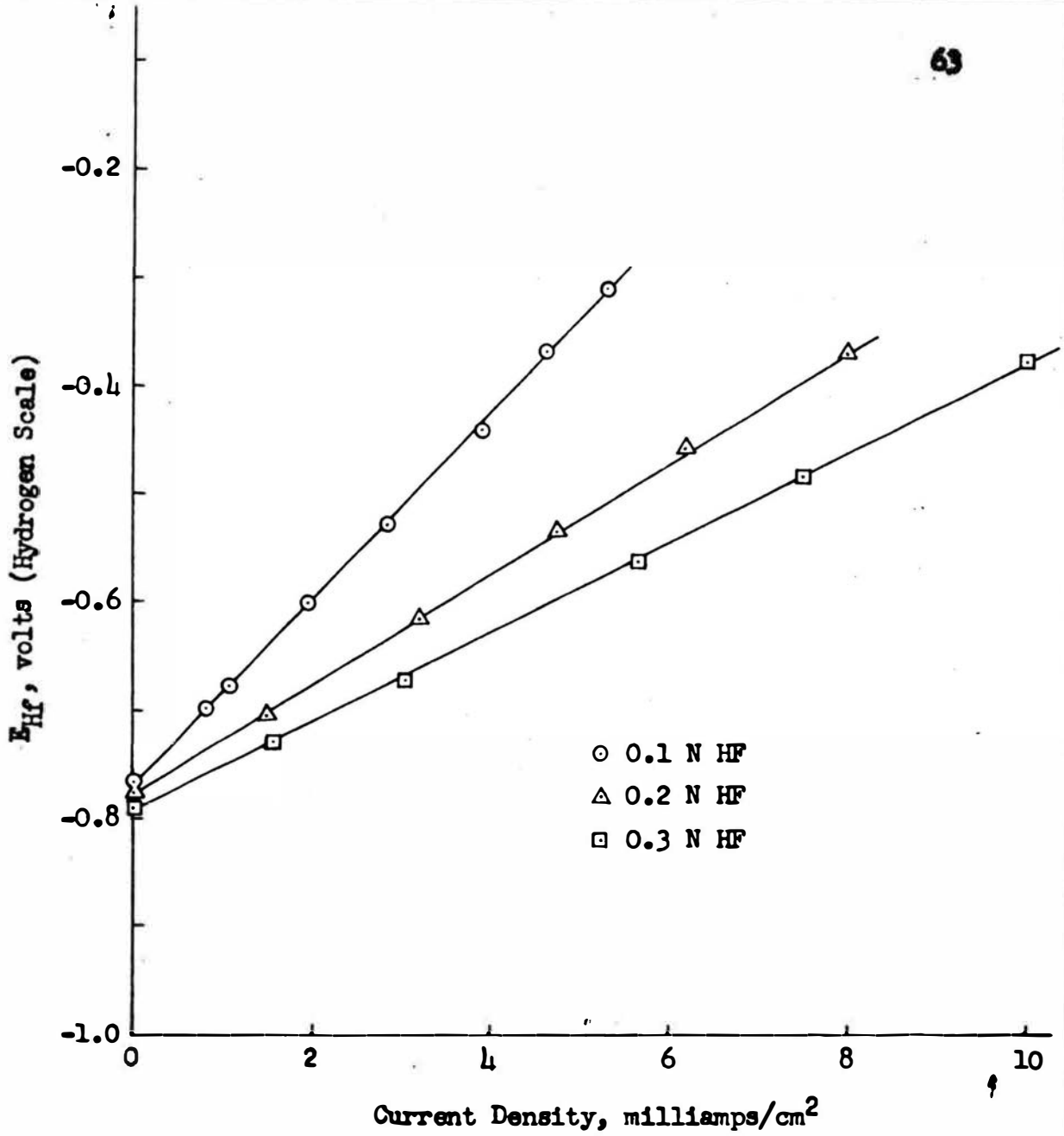

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Figure No. 28. Dissolution Potentials Developed by Hafnium Electrode Dissolving Anodically in Hydrofluoric Acid at 25°C with Different Current Densities.

SCALE:	DATE	CASE NO:
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APPROVED BY:		SHEET NO:

the dissolution is directly proportional to the current density for a given hydrofluoric acid concentration and that the potential becomes less noble as the hydrofluoric acid concentration increases.

Sample Calculations. The calculations are the same as those given for the dissolution potentials on pages 51 and 55.

CHAPTER IV

DISCUSSION

I. THE KINETIC BEHAVIOR OF HAFNIUM IN HYDROFLUORIC ACID

The Reaction Rate

The reaction rate of hafnium with hydrofluoric acid, according to the net stoichiometry of the equation,

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2 \qquad (3)$$

was determined over concentration ranges from 0.05 to 1.00 N HF and temperature ranges from 5 to 50°C. The reaction was carried out in both hydrofluoric acid and hydrofluoric-1.00 N hydrochloric acid mixtures. The hydrochloric acid was used to suppress the ionization,

$$HF \rightleftharpoons H^+ + F^- \qquad (K_{25°C} = 6.71 \times 10^{-4}), \qquad (6)$$

thereby increasing the unionized hydrofluoric acid concentration, HF_{un}, and controlling the equilibrium concentration of fluoride complexes such as HfF_3^{+1}, HfF_5^{-1}, HfF_6^{-2}, and HfF_7^{-3}.[4] Calculations with the above equilibrium constant show that 0.05 N hydrofluoric acid is approximately ten per cent ionized, 1.00 N hydrofluoric acid is about three per cent ionized, and in the presence of 1.00 N hydrochloric acid (assuming the HCl is one hundred per cent ionized), hydrofluoric acid in concentrations from 0.05 to 1.00 N is less than 0.5 per cent ionized.

The reaction rate was found to be directly proportional to the unionized HF concentration raised to the first power, ie., a first

order reaction. This same proportionality and order was observed in hydrofluoric-1.00 N hydrochloric acid mixtures. Studies were made in which the hydrochloric acid concentration was varied from 0 to 8 N in 0.300 N hydrofluoric acid. These showed a definate rate increase with HCl concentration in regions where the HF_{un} concentration would not be increased by an equilibrium shift (0.300 N hydrofluoric acid is only about one per cent ionized in acid mixtures containing 0.5 N HCl). Therefore, increasing the HCl concentration from 0.5 to 6 N should only increase the rate about one per cent due to the increase in the HF_{un} concentration. However, a rate increase of about twenty-five per cent was observed. This prompted studies using sulfuric acid in 0.300 N hydrofluoric acid to see if the rate increase was due to some environmental factors peculiar to hydrochloric acid or to a hydrogen ion effect. By varying the sulfuric acid concentration from 0 to 8 N, it was found the sulfuric acid did increase the rate, but only to the extent that might be predicted by the equilibrium shift towards the HF_{un}. Thus, the increase caused by the hydrochloric acid can be attributed to an environmental effect, possibly on the media through which diffusion takes place, solubility of reaction products, or transformation of films on the metal surface, rather than a hydrogen ion effect.

The reaction rate increased with stirring speed, being linear over a large part of the range investigated. The leveling-off at the higher stirring speeds was probably due to the limit of the stirring efficiency for this particular system.

The activation energy for the reaction was found to be 5.3 ± 0.1 kcal in hydrofluoric acid and 5.4 ± 0.1 kcal in hydrofluoric-1.00 N hydrochloric acid mixtures. (The calculation of the deviation or error for the activation energy is shown in Appendix E, page 212.) This close agreement indicates that the controlling dissolution mechanism is relatively unaffected by the presence of the hydrochloric acid.

Moelwyn-Hughes[17] states that heterogeneous reactions between a solid and liquid that are diffusion controlled usually have three characteristics: (1) the reaction is first order, (2) the activation energy is about 4.5 kcal, and (3) the reaction rate varies with the rate that the solution is stirred. This reaction has been described by Nernst[18] as one in which the chemical reaction proper takes place very rapidly at the solid surface, the liquid in the immediate neighborhood soon becoming choked with reaction products and hindering further chemical change. Fresh molecules of reactant can, however, diffuse slowly through this product or diffusion layer, with a velocity which is small compared with that of the chemical change and which diminishes as the concentration of the reacted substance falls off.

These characteristics very readily describe the dissolution reaction of hafnium in hydrofluoric acid. This same type of reaction was previously found for the dissolution of zirconium in hydrofluoric acid.[3,4,5,6,7] The one variation is the activation energy, in which the experimental value is slightly higher than the theoretical value

(5.3 kcal compared to 4.5 kcal). The difference can possibly be explained by the derivation of the theoretical value. (The calculated value of the experimental error is approximately one-tenth kcal, so this would not account for the variation.) The theoretical value of the activation energy results from equating the reaction rate to the diffusion rate of the reactant through a liquid film to the metal surface as described by Fick's law. The assumptions that the concentration gradient is equal to the concentration of the bulk solution divided by the thickness of the diffusion layer and the thickness of the diffusion layer is independent of temperature lead to the temperature coefficient for the reaction rate constant (activation energy) being equal to that for the diffusion coefficient which is observed to be about 4.5 kcal at 25°C. There is enough uncertainty in these assumptions to possibly account for the variation, but supposing it to be real, it may be explained in a different manner as suggested by James, et al.,[7] for the relatively high activation energies of zirconium dissolving in HF-HNO_3 mixtures reported by Vander Wall and Whitner[6]. From examining the oxidation potential of hafnium, it seems probable that in a manner similar to aluminum, the metal is protected from corrosion by some type of thin adherent film (probably oxide or hydride). Kortüm and Bockris say this chemical passivity of active metals can be produced by formation of adherent, very thin, invisible layers of metallic oxide upon exposure to atmospheric oxygen.[19] Activations of these passive surfaces have indicated that this phenomenon depends only upon a monomolecular layer

of oxide, thus as long as the oxide is not attacked, the film cannot grow and always remains invisible. Kuhn points out from his observations on zirconium corroding in hydrochloric acid, that once the corrosion process has started in solution, a hydride film is formed on the metal surface.[20] This was also observed on zirconium corroding in hydrofluoric acid by James, et al.[5,7] James and Straumanis point out that the thin grayish film observed on hafnium dissolving in dilute hydrofluoric acid (0.1 N) is probably a hydride.[32] Thus, during dissolution, there is probably always a film on the hafnium surface, originally an oxide, but replaced by a hydride film when hydrofluoric acid reacts with the metal. Therefore, to react with the metal, the HF molecules must be diffusing through a film which is possibly non-permeable to other molecules. This film could be acting as another resistance to the diffusion process, thereby increasing the activation energy.

Influence of Various Additives on the Rate

Small additions (approximately 0.01 M) of K^+, Cl^-, NO_3^-, Br^-, and $C_6H_5O_7^{-3}$ (citrate) had no detectable effect on the rate.

Fluoride Salt Additions. Low concentrations of fluoride salts in hydrofluoric acid increased the reaction rate appreciably. This can be explained simply by an increase in the HF_{un} concentration due to a shift in the equilibrium. Large concentrations of fluoride salts in hydrofluoric acid decreased the reaction rate by the formation of insoluble salt films on the metal surface. Sodium fluoride was the

most effective, producing almost complete passivation in solutions with concentrations above 0.15 M NaF. This salt film was tentatively identified as sodium fluohafnate, Na_3HfF_7, by x-ray analysis. Sodium chloride additions above this concentration also produced passivation, indicating that the sodium cation was responsible for the insoluble salt. Similar runs were made with sodium fluoride additions in 0.304 N hydrofluoric-1.00 N hydrochloric acid mixture. Passivation was not obtained until the NaF concentration reached 0.80 M. This was apparently due to the increased solubility of the sodium fluohafnate in the hydrochloric acid.

It was interesting to note that the salt concentration necessary for passivation in hydrofluoric acid increased in the same order as the cation size, suggesting the same solubility pattern as was observed in similar studies with zirconium.[5] An attempt was made to test the pattern further with the lithium cation. However, it was impossible to obtain passivating concentrations of the lithium ion due to the solubility limit of lithium fluoride.

Noble Metal Salt Additions. The addition of equivalent amounts of noble metal ions (0.005 N) produced some passivation in each case, the effectiveness increasing in the order--gold, silver, and platinum. In each case, the reconstituted noble metal was found in the reactor and the hafnium specimen had a shiny surface. The shiny surface quickly disappeared when placed in fresh hydrofluoric acid (replaced by the usual gray surface), indicating that it was not the

plated-out noble metal. Buck, et al., found that the corrosion rate of titanium coupled to platinum metal was greatly decreased in boiling 2 M hydrochloric acid.[21] Titanium dioxide was found at the points of contact between the two metals in quantities that could be identified. They suggest that platinum protects titanium because it facilitates the formation of a protective oxide film on the titanium surface. This present situation is not unlike the one described by Buck. Titanium and hafnium are similar metals (in reactive respects) and since the noble metal ions from the additions must have been reduced at or very near the hafnium surface, they could have acted as couples or cathodes (effectively as oxidizing agents) and promoted oxide film formation. Thus the shiny films were probably oxides and caused passivation by increasing the thickness of an existant layer or forming new layers through which the HF_{un} had to diffuse. It will be discussed later with the difference effect that anodic currents have a very pronounced effect on the dissolution rate, probably through the formation of surface films. The observed passivation occurs as a consequence of the tendency of the noble metal to promote the electrochemical reaction. When the noble metal is removed from the solution, the passivation disappears.

The inability of the platinum ions to passivate the hafnium surface in the hydrofluoric-1.00 N hydrochloric acid mixture was probably due to some environmental factors affecting the formation of the oxide or liquid boundary layer. The shiny surface was formed in this case, but apparently more permeable than in hydrofluoric

acid alone. Bockris mentions that certain anions, notably halides, often prevent passivation when added to solutions in which passivation is otherwise readily attainable.[22] He suggests that these ions may be preferentially adsorbed on the metal surface, preventing the adsorption of "passivating" ions.

Although the addition of the noble metal ions did not rule out the possibility of an electrochemical reaction on the surface of the metal, it did seem to point out that this was not the predominant reaction. If the rate controlling step was electrochemical, the noble metal additions would have promoted local cathode formation on the hafnium surface with possibly an accompanying increase in rate, but certainly not the observed decrease. Further evidence that the reaction is not electrochemically controlled is the fact that the reaction rate was unaffected by removal of the filament core around which the crystal bar was grown. Impurities in the metal concentrated at the core boundary would cause a highly cathodic area that should appreciably affect any electrochemical controlled reaction.

Oxidizing Agent Additions. The addition of equivalent amounts of oxidizing agents showed that some passivation was caused by each, their effectiveness increasing in the order—$NaBiO_3$, $KMnO_4$, and $K_2Cr_2O_7$. Again, this passivation was most likely caused by the formation of oxide films on the metal surface, promoted by the oxidizing agents. The metal surface resulting from these additions had a shiny appearance similar to other metals known to have passive

oxide coatings[23] and to the shiny surfaces resulting from the noble metal salt additions. When the passivated metal surface was placed in fresh hydrofluoric acid, the reaction appeared to resume at or near its original rate, indicating the oxide coating on the passivated surface was removed or altered by the reaction with HF. A thin oxide coating could be reformed by the metal reacting with dissolved oxygen or water, or alternatively, a hydride film might be formed from hydrogen reacting at the metal surface.[32] Smith and Hill found that the presence of dissolved oxygen in hydrofluoric acid did not measurably affect the corrosion rate of zirconium[4], so there is no reason to suspect it would affect the corrosion rate of hafnium. Kuhn has reported that the "breakaway" corrosion of normally passive zirconium in hydrochloric acid is promoted by hydride films forming under the protective oxide coating.[20] The stress caused by the hydride starts loosening and flaking-away the oxide film. The hydride films offer only limited corrosion protection with their ability to hinder diffusion, thus, the reaction proceeds. This seems to point out that the reaction between the hafnium metal and water to reform the oxide film plays only a minor part in the normal dissolution in hydrofluoric acid, and that the major reaction is diffusion through a hydride film. Now a hypothesis is allowed as to the reactions on the metal surface and the sequence in which they may occur:

Step 1: Initiation of the dissolution reaction by attack on (or diffusion through) the protective oxide layer by unionized HF.

$$HfO_w + 4\ HF \longrightarrow HfF_4 + (2 - w)\ H_2 + w\ H_2O$$

Step 2: Reaction of the metal with $H^{\cdot}$ and H_2O to form surface films.

$$Hf + x\ H^{\cdot} \longrightarrow HfH_x$$

$$Hf + y\ H_2O \longrightarrow HfO_y + y\ H_2$$

Step 3: Dissolution of the metal by HF and H^+ diffusing through the surface films.

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2 \qquad \text{(chemical)}$$

$$Hf + 4\ H^+ \longrightarrow Hf^{+4} + 2\ H_2 \qquad \text{(electrochemical)}$$

Considering the effects of the noble metal salt additions, and the work of James, et al.,[7] Kuhn,[20] and Smith and Hill,[4] it appears that the last reaction in steps 2 and 3 may make only minor contributions under normal dissolution conditions, ie., only in hydrofluoric acid. Whichever way the reaction proceeds, equal amounts of hydrogen are formed (once the hydride film is formed), and the reaction is dependent on the rate that HF_{un} diffuses to the metal surface.

Mineral Acid Additions. Small additions (0.10 N) of mineral acids in 0.300 N HF did not markedly affect the dissolution rate of hafnium. It appeared though, that the hydrochloric acid addition caused a slight increase in the rate, the sulfuric acid no noticeable effect, and the phosphoric acid a slight decrease. The effect of hydrochloric and sulfuric acid was further investigated and discussed previously in this section.

Some qualitative studies were made in very dilute hydrofluoric acid (0.003 to 0.015 N HF) with hydrochloric additions. No hydrogen

could be seen evolving from a piece of hafnium in 0.003 N HF. However, when concentrated hydrochloric acid was added (making the solution 3 N HCl), hydrogen immediately began evolving from the metal surface. Pieces of hafnium were also put in 0.003 N HF-3 N HCl, 0.007 N HF-3 N HCl, and 0.015 N HF-3 N HCl acid mixtures. Hydrogen was evolved from the hafnium surface in each case. When concentrated hydrochloric acid was added, making the solutions 6 N HCl, the hydrogen evolution rate appeared to remain about constant or increase very slightly. No reaction at all could be detected in concentrated (12 N) hydrochloric acid alone. These observations tend to emphasize the predominant role played by the unionized HF and the minor part of the hydrogen ions.

II. ANODIC BEHAVIOR OF HAFNIUM IN HYDROFLUORIC ACID

It should be pointed out in beginning, that the rate studies and the electrochemical studies were probably different aspects of a total reaction and that one may not necessarily substantiate or confirm the other under similar circumstances.

The rate studies were measured on a rotating specimen with the face sloped back at a forty-five degree angle from the bottom leading horizontal edge. Hence, the fluid passed vertically across the metal face. The electrochemical studies were made with a vertical stationary electrode and adjacent stirring, causing the major part of the fluid to pass horizontally across the metal face. In all

probability, this led to different stirring efficiencies, but differences in the liquid films on the metal surface should have been small.

The rate studies concerned the over-all reaction, which is possibly a combination of rates of simultaneously occurring reactions, both chemical and electrochemical. The electrochemical study deals solely with the electrochemical reaction and the things that affect it. It should be kept in mind that evidence in the rate studies indicated that the electrochemical reaction makes only a minor contribution under normal dissolution conditions.

The Difference Effect

The difference effect was observed in a series of HF concentrations in hydrofluoric-1.00 N hydrochloric acid mixtures and at various current densities. This yielded information as to the effect of anodic polarization on the hafnium electrode during dissolution. The results obtained indicated that the difference effect was a function of current density and independent of hydrofluoric acid concentration. This was previously observed in studies on Ti,[24] Al,[25,26] Zn,[27] and Zr[8].

The resulting expression for the difference effect was:

$$\Delta = KI = (10.0 \pm 0.3)\ I \qquad (5)$$

A value of K = 6.97 in the above equation would mean that the hafnium electrode is one hundred per cent polarizable or that a current flowing from the hafnium electrode decreases the hydrogen evolution

from the metal surface by an amount electrochemically equivalent to the current. A value of K = 10.0 means the hafnium electrode is polarizable to an extent greater than one hundred per cent, ie., an anodic current decreases the hydrogen evolution from the metal surface by an amount greater than that equivalent to the current. For example, an anodic current of one milliamp would not only decrease the hydrogen evolution by 6.97 mm^3 (the hydrogen equivalent of the current) but also by an additional 10.0 - 6.97 or approximately 3 mm^3. This indicates that the normal dissolution conditions are changed by allowing a current to flow through the electrode and can be explained by some change taking place in the electrode reaction (or conditions) due to the current. The present thought is that the flowing current promotes an oxide film formation on the electrode surface that tends to passivate it. This would also explain the unusual report from Stern that alloying titanium with as little as one-tenth per cent of palladium reduces its corrosion potential by ninety-eight per cent.[28] The palladium nuclei would act as local cathodes or couples, producing an anodic current which in turn would alter the surface conditions, causing a protective oxide film to form that retards further corrosion. Any subsequent reaction would electrochemically produce hydrogen at the cathodes where it would be liberated. This would prevent the hydride from forming underneath the oxide film, disrupting its protective role.

A similar situation exists in the report from Stern and Bishop that a small spot of platinum on a tantalum surface protects more than 10,000 times its own area from hydrogen embrittlement in concentrated hydrochloric acid for more than 1,000 hours, which when unprotected, becomes embrittled in only a few hours.[29] Again the platinum would act as a cathode for the liberation of hydrogen, not only keeping hydrogen away from the tantalum, but also promoting formation of protective films that further reduce hydrogen formation.

Work by Straumanis and Chen[24] and Straumanis, James, and Ratliff[30] on the difference effect in hydrofluoric acid on titanium and alpha solid solutions of oxygen in titanium gave values of K = 5.7 for the pure metal and approximately 9.5 for alloys containing five to ten per cent oxygen. Similar work on zirconium by Straumanis, James, and Custead[31] gave a value of K = 10.5 for the metal (containing 1.52 per cent oxygen) and approximately 11.8 for alloys containing three to seven per cent oxygen. These are the few cases where this extreme anodic polarization (values of K greater than 6.97) has been found. It seems that the unusual anodic behavior of these reactive metals may be associated with oxides on the metal surface and that corrosion occurs when the oxide film is attacked and replaced with a hydride film. As long as the reaction proceeds chemically with HF, the hydride film is stable, but once anodic currents begin, conditions favor the oxide formation, thereby changing the surface to a more passive condition. Under these conditions, the slower reaction takes place when something, such as hydrofluoric

acid, is present to dissolve the oxide or to remove the oxide film at points of strain or imperfections so that "breakaway" corrosion can be initiated. This might explain the higher K values of the oxygen alloys, too. They already have a partial oxide film built into them, making them more susceptible to anodic polarization as they would not be completely dependent on environmental conditions for the formation of the passive film.

The Dissolution Potentials

The dissolution potentials of hafnium were highly negative and became more negative (less noble) with increasing hydrofluoric acid concentration. They became more positive with time, approaching constant values in about one hour. This agrees with previous work on zirconium in hydrofluoric acid.[5] However, contrary to this, the dissolution potentials became more noble in hydrofluoric-hydrochloric acid mixtures while the total dissolution rate was observed to increase. Two possible explanations of this increase are possible. The slow step according to the rate studies involves the diffusion of unionized HF to the metal surface (through surface films in many or all instances). If the HF diffuses to the metal surface and upon reaction partially removes some of the surface film, uncovered impurities acting as local cathodes would be made available to hydrogen ions, causing the rate to increase. The potential might then become more noble because the strong difference effect would prevail over the opposing effect of the local cathodes. However, the

absence of rate increases in sulfuric acid mixtures seems to eliminate this explanation. The second alternative is that the hydrochloric acid allows diffusion to take place more readily through the liquid layer, or reduces the thickness or increases the porosity of the surface films so that HF more readily comes in contact with the metal atoms. Again, it might be mentioned that halide ions are known to prevent passivation apparently due to their adsorption on metal surfaces.[22] This would certainly affect the formation of the surface films and might even in itself cause the potential to become more noble.

Influence of Various Additives.

1. Fluoride Salt Additions. The dissolution potentials became less noble upon addition of the fluoride salts in concentrations that caused passivation of the metal in the rate studies. The order of the decrease in the potentials corresponded to the concentration of the salt, ie., ammonium fluoride which was present in the highest concentration caused the largest decrease in potential. Even though the salt layer was effective in decreasing the area of the reaction surface to retard the over-all rate, some local cathodes were still active so that the dissolution potentials decreased. The decreases were about what would be expected from an increase in the hydrofluoric acid concentration.

2. Noble Metal Salt Additions. Platinum and gold chloride additions made the dissolution potentials more noble. The silver

nitrate addition did not seem to affect the potential. These results, however, were not reproducible and should be considered semi-quantitative. It was interesting to note, though, the gold addition that caused the largest increase in potential resulted in a very shiny and apparently relatively thick (oxide) film. In this case, the thicker coating must have effectively covered the entire surface, including local cathodes, so that the potential became more noble. The thicker coating would also have caused the observed decrease in the dissolution rate and could have been formed as previously mentioned in the kinetic discussion.

3. Oxidizing Agent Additions. It was previously postulated that the oxidizing agents decreased the total dissolution rate by promotion of oxide films on the metal surface. It was observed that the dissolution potentials were slightly decreased by oxidizing agents (if an exception is made of the bismuthate addition because of the precipitate formation which could have affected the potential). This is compatible with previous postulations for the mechanism if the (oxide) films that caused the rate decrease were discontinuous and did not cover all the local cathodes. Potassium permanganate and potassium dichromate are known to be depolarizers that could cause the observed potential decreases. There was visual evidence to support this in that the films from the oxidizing agent additions were not as shiny as those from the noble metal salt additions indicating they were either not as thick or as dense.

4. Mineral Acid Additions. That hydrochloric acid caused the dissolution potentials to become more noble has been previously discussed. Small additions of sulfuric and phosphoric acid had no noticeable effect on the potentials.

Influence of Current Density. A strong influence of current density was observed on the dissolution potentials in HF. The effect was greater at lower hydrofluoric acid concentrations. This confirms the large influence of current density on polarization suggested by the positive difference effect. The anodic current shifts the potential to more noble values that would in itself lower the self-dissolution rate. This indicates that small additions of noble metals to hafnium would increase its anti-corrosive properties in a way similar to those cases reported by Stern[28,29] that were discussed previously.

CHAPTER V

RECOMMENDATIONS

In this investigation, the kinetic and electrochemical studies were made with different geometrical set-ups. The rate specimens were rotated and the difference effect and potential study specimens (electrodes) were stationary. As these factors could have some effect for diffusion controlled processes, future kinetic studies might be made with fixed specimens. The geometrical set-ups for this study were chosen so the results could be compared with previous work on titanium and zirconium. Originally, the idea of the rotating sample for the kinetic study was used because of its effectiveness in removing hydrogen from the sample, thereby minimizing polarization.

Of particular interest would be the determination of activation energies in the presence of oxidizing agents and higher concentrations of mineral acids. These might help clarify the formation of surface films and their role as resistances to diffusion. These studies should also include the effect of other mineral acids on the rate.

Other studies that might be enlightening would be the effect of various additions to the solvent on the current density developed by the hafnium electrode. Also, studies on hafnium alloyed with oxygen, nitrogen, and platinum might give further insight into the roles of oxide films and noble metal couples in the corrosion of the active metals.

A direct method of following the reaction rate would be helpful and reassuring. The indirect (gas evolution) method could be very misleading if under some conditions it did not accurately indicate the true dissolution rate. At the present time, an apparatus has been designed to directly measure the corrosion rate of metals in liquid media. Radioactive metals will be used and the corrosion rate will be followed by measuring the rate of concentration increase of the radioactive ions in solution with a scintillation counter and rate meter. The reaction system is of the tank-flow type and constructed so that all parts in contact with the corrosive media are polyvinyl chloride, teflon, or lucite. This apparatus will not only give a check on the gas evolution equipment, but will be used for corrosive media in which the composition of the products may be non-gaseous or gases of variable composition.

CHAPTER VI

LIMITATIONS

Gaseous Products

Straumanis and Ballass[1] found that the hydrogen evolved was equivalent to the hafnium dissolved during its dissolution in hydrofluoric acid. However, this might be questionable in the case of some of the additions that were made. For instance, in the presence of the oxidizing agents, some hydrogen could have been oxidized to water, making the dissolution reaction appear to be slower than it actually was.

Sample Area

The dimensions of the hafnium specimen (sample) were measured accurately with a micrometer caliper and the calculated surface area of the exposed face assumed to be the effective surface area of the sample. On a molecular scale, the effective surface area in all probability was several times this value. However, the surface was prepared in the same manner before each run, so the effective area should have been about the same each time. For first order diffusion reactions, the effective area appears to remain constant as the reaction progresses even though the actual surface becomes eroded.[17]

Rates

An important limitation is that the rate data is not absolute, preventing calculation of absolute reaction rate constants and the

accompanying thermodynamic data. It appears that any effort in this direction must be directed from the electrochemical side, possibly through irreversible electrode potentials. Future work on this is anticipated.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The rates of dissolution, difference effect, and dissolution potentials of hafnium were determined in hydrofluoric acid.

The dissolution rates were determined by collection and periodic measurement of the volume of gas liberated from a hafnium specimen according to the net stoichiometry of the equation:

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2$$

The hydrofluoric acid concentration was varied from 0.05 to 1.00 N. The temperature was varied from 5 to 50°C. The effect of stirring speed was also studied. These led to the following:

1. The hafnium-hydrofluoric acid reaction is first order with respect to the concentration of unionized HF over the range studied.

2. The activation energy for the dissolution reaction is 5.3 ± 0.2 kcal.

3. The reaction rate is directly proportional to the speed at which the hafnium specimen is rotated in the stirring speed range of 100 to 400 revolutions per minute.

On the basis of the above, it was concluded that the dissolution of hafnium in hydrofluoric acid is a diffusion controlled reaction.

Additions of fluoride salts, noble metal salts, oxidizing agents, and mineral acids were made to determine their effect on the dissolution rate. They indicated that:

1. Fluoride salt additions increase the dissolution rate (by an equilibrium shift towards unionized HF) until a critical cation concentration is reached where the hafnium is passivated by the formation of insoluble salt films on the surface.

2. Noble metal salt additions (0.005 N) tend to passivate the hafnium by the formation of films (presumably oxide) on the surface promoted by reduction of the noble metal ions.

3. Oxidizing agents (0.0529 N) tend to passivate the hafnium by promotion of films (presumably oxide) on the surface.

4. Mineral acid additions show no consistent trend. Hydrochloric acid (0 to 8 N) tends to increase the rate, sulfuric acid (0 to 8 N) shows no appreciable effect other than the equilibrium shift towards the unionized HF, and phosphoric acid (0.10 N) retards the reaction slightly.

The difference effect measurements resulted in the following:

1. The difference effect is directly proportional to the current density and independent of the hydrofluoric acid concentration.

2. Anodic currents have a very strong polarizing influence on the dissolution reaction.

The dissolution potentials of hafnium became less noble as the hydrofluoric acid concentration was increased. Additions of fluoride salts, noble metal salts, oxidizing agents, and mineral acids showed that:

1. Fluoride salt additions in concentrations sufficient to give passivation cause the potential to become less noble.

2. Platinum and gold chloride additions (0.005 N) tend to make the potential more noble. Silver nitrate addition (0.005 N) had no effect on the potential.

3. Oxidizing agent additions (0.0529 N $KMnO_4$ and 0.0529 N $K_2Cr_2O_7$) tend to make the potential less noble.

4. Mineral acid additions show no consistent trend. Hydrochloric acid (0 to 2 N) tends to make the potentials more noble. Sulfuric and phosphoric acid (0.10 N) show no noticeable effect.

Surface reactions for the dissolution are proposed as follows:

Step 1: Initiation of the dissolution reaction by attack on (or diffusion through) the protective oxide layer by unionized HF.

$$HfO_w + 4\ HF \longrightarrow HfF_4 + (2 - w)\ H_2 + w\ H_2O$$

Step 2: Reaction of the metal with H° and H_2O to form surface films.

$$Hf + x\ H^\circ \longrightarrow HfH_x$$

$$Hf + y\ H_2O \longrightarrow HfO_y + y\ H_2$$

Step 3: Dissolution of the metal by HF and H^+ diffusing through the surface films.

$$Hf + 4\ HF \longrightarrow HfF_4 + 2\ H_2 \qquad \text{(chemical)}$$

$$Hf + 4\ H^+ \longrightarrow Hf^{+4} + 2\ H_2 \qquad \text{(electrochemical)}$$

Evidence indicates that the reaction of the metal with H_2O and H^+ (the last reaction in steps 2 and 3) make only minor contributions to the total rate in the normal dissolution of the metal in hydrofluoric acid. The diffusion of the unionized HF to the reacting surface is the rate controlling step.

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BIBLIOGRAPHY

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APPENDIX A

APPENDIX A

MATERIALS

The following is a list of the major materials used in this investigation. More information on these commercially available materials may be found by consulting the chemical catalogue of the company concerned.

1. Acid, Hydrochloric. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

2. Acid, Hydrofluoric. Reagent grade, meets ACS specifications. Merck and Company, Rahway, N. J.

3. Acid, Oxalic. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

4. Acid, Phosphoric. Reagent grade. General Chemical Company, New York, N. Y.

5. Acid, Sulfuric. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

6. Ammonium Fluoride. Reagent grade. Allied Chemical Corporation, New York, N. Y.

7. Gold Chloride. Purified. Fisher Scientific Company, Fair Lawn, N. J.

8. Hafnium. Crystal bar, obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. Typical analysis (ppm): Ag, <1; Al, 1; B, 0.3; Ba, 3; Be, 0.2; Ca, 10; Cd, 0.2; Co, 1; Cr, 12; Cu, 3; Fe, 50; K, <40; Li, <0.2; Mg, <2; Mn, <1; Mo, <4; Na, <5; Ni, 3;

P, <100; Pb, <1; Si, <2; Sn, <1; Ti, <2; V, <2; Zn, <100; Zr (HfO_2 std.), 70,000; Zr (liquid stds.), 38-42,000; O, 90-110; C, 30; and H, 10-20. Westinghouse Atomic Power Division, Pittsburgh, Pa.

9. Lithium Sulfate. Reagent grade. Allied Chemical Corporation, New York, N. Y.

10. Mercurous Chloride. Reagent grade, meets ACS specifications. Merck and Company, Rahway, N. J.

11. Mercury. Technical. J. T. Baker Chemical Company, Phillipsburg, N. J.

12. Platinum Chloride. Analytical Reagent. Mallinckrodt Chemical Works, St. Louis, Mo.

13. Potassium Chloride. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

14. Potassium Dichromate. Reagent grade, meets ACS specifications. Merck and Company, Rahway, N. J.

15. Potassium Fluoride. Technical. Harshaw Scientific, Cleveland, Ohio.

16. Potassium Iodide. Analytical Reagent, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Mo.

17. Potassium Permanganate. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

18. Silver Nitrate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

19. Sodium Bismuthate. Reagent grade, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Mo.

20. Sodium Bromide. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N. Y.

21. Sodium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

22. Sodium Citrate. U. S. P. Chas. Pfizer and Company, New York, N. Y.

23. Sodium Fluoride. Reagent grade, meets ACS specifications. Merck and Company, Fair Lawn, N. J.

24. Sodium Hydroxide. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

25. Sodium Nitrate. Reagent grade, meets ACS specifications. J. T. Baker Chemical Company, Phillipsburg, N. J.

APPENDIX B

APPENDIX B

APPARATUS

The following is a list of the major components of the apparatus used in this investigation.

Mounting and Surface Preparation of Hafnium Specimens

1. Belt Surfacer. Buehler No. 1250. Buehler Ltd., Evanston, Ill.

2. Centermet Press. One-inch mold, Buehler No. 1305. Buehler, Ltd., Evanston, Ill.

3. Hand Grinder. Handimet, 4-stage, Buehler No. 1470. Buehler, Ltd., Evanston, Ill.

Gas Evolution Apparatus

1. Burette, Gas. Graduated from 0 to 100 ml in 0.2 ml divisions.

2. Flask, Distilling. Three-neck, 500 ml, center joint 34/45, side joints 24/40.

3. Heater, Immersion. Knife-blade type, 115 v, 500 w, ac. Centeral Scientific Co., Chicago, Ill.

4. Motor, Stirrer (Reactor). Fultork Labmotor, 115 v, 60 c, ac. Fisher Scientific Co., Pittsburg, Pa.

5. Stirrer (Water Bath). Pensky-Martens Motor Stirrer, 115 v, 60 c, ac. Fisher Scientific Co., Pittsburg, Pa.

6. Switch, Relay. Type SR600A, 115 v, ac. Philadelphia Scientific Glass, Quakertown, Pa.

7. Thermoregulator. Type SE-712. Philadelphia Scientific Glass, Quakertown, Pa.

Difference Effect Apparatus

1. Ammeter. Model 931. Weston Electric Instrument Corporation, Newark, N. J.

2. Battery, Storage. Six-volt.

3. Burette, Gas. Graduated from 0 to 100 ml in 0.1 ml divisions.

4. Flask, Distilling. Three-neck, 500 ml, center joint 34/45, side joints 24/40.

5. Heater, Immersion. Knife-blade type, 115 v, 500 w, ac. Centeral Scientific Co., Chicago, Ill.

6. Motor, Stirrer (Reactor). Sargent cone-drive stirring motor, 115 v, 60 c, ac. E. H. Sargent and Co., Chicago, Ill.

7. Motor, Stirrer (Water Bath). No. 18835, 115 v, 60 c, ac. Centeral Scientific Co., New York, N. Y.

8. Resistance Box. Graduated from 0 to 9999 ohms in 1 ohm divisions. Centeral Scientific Co., Chicago, Ill.

9. Switch, Relay. Six v, dc. Struthers-Dunn, Inc., Philadelphia, Pa.

10. Thermoregulator. Mercural type. Made by Dr. T. Ejima, Metallurgy Dept., Missouri School of Mines and Metallurgy, Rolla, Mo.

Dissolution Potential Apparatus

1. Ammeter. Model 931. Weston Electric Instrument Corporation, Newark, N. J.

2. Cells, Dry. General purpose, 1.5 v.

3. Galvanometer. No. 2420C. Leeds and Northrup Co., Philadelphia, Pa.

4. Heater, Immersion. Knife-blade type, 115 v, 500 w, ac. Centeral Scientific Co., Chicago, Ill.

5. Motor, Stirrer (Reactor). Fultork Labmotor, 115 v, 60 c, ac. Fisher Scientific Co., Pittsburg, Pa.

6. Motor, Stirrer (Water Bath). Sargent cone-drive stirring motor, 115 v, 60 c, ac. E. H. Sargent and Co., Chicago, Ill.

7. Potentiometer. No. 7651. Leeds and Northrup Co., Philadelphia, Pa.

8. Resistance Box. Graduated from 0 to 999.9 ohms in 0.1 ohm divisions. Centeral Scientific Co., Chicago, Ill.

9. Standard Cell. Eplab Students' Cell. The Eppley Laboratory, Inc., Newport, R. I.

10. Switch, Relay. Type SR600A, 115 v, ac. Philadelphia Scientific Glass, Quakertown, Pa.

11. Thermoregulator. Type SE-712. Philadelphia Scientific Glass, Quakertown, Pa.

Miscellaneous Special Equipment

1. Beakers, Polyethylene. 250 and 600 ml capacity.

2. Burette, Polystyrene. Graduated from 0 to 50 ml in 0.1 ml divisions.

3. Cylinder, Graduated, Polyethylene. Graduated from 0 to 300 ml in 25 ml divisions.

APPENDIX C

APPENDIX C

EXPERIMENTAL PROCEDURE

Measurement of the Dissolution Rate of Hafnium in Hydrofluoric Acid and Hydrofluoric-Hydrochloric Acid Mixture

The procedure for this part of the experimentation follows as a step-by-step operation procedure. Refer to Figure 1, page 10, to clarify the nomenclature pertaining to the apparatus.

1. Start the constant temperature bath by (a) turning on the cooling water and the water bath stirrer, and (b) plugging the extension cord from the relay switch into a 115 volt ac source which both activates the thermoregulator and supplies current for the knife-blade heater. The thermoregulator must be set to maintain the water bath temperature at the level desired for the run.
2. Remove the mercury seal assembly, including the combination PVC stirrer foot and the hafnium sample holder.
3. Place 300 ml of hydrofluoric acid (or hydrofluoric-hydrochloric acid mixture) of the desired concentration in the wax-lined reaction flask. Add the acid through a polyethylene funnel to prevent it from contacting portions of the flask not covered with wax. Cover the flask and allow it to set in the water bath for approximately two hours to bring the system to bath temperature before starting the run.

4. Attach a lucite-mounted hafnium sample with a freshly prepared surface to the stirrer foot with melted beeswax. The stirrer foot is constructed so that the hafnium sample is always attached at an equal distance from the axis of rotation and the exposed hafnium surface is inclined at an angle of 45° to the direction of rotation. The directions for preparing and mounting the hafnium specimen in lucite and for preparing the hafnium surface previous to a run are given in Appendices F and G, pages 218 to 225.
5. Etch the hafnium sample for 10 to 20 seconds in hydrofluoric acid of the concentration to be used in the run (until hydrogen is being evolved from the entire surface), rinse with distilled water and allow to drain.
6. Adjust the leveling bulb so that the water level in the gas burette is zero.
7. Open stopcock at point J.
8. Put stopcock grease on the glass joint of the mercury seal to insure a gas-tight seal when it is inserted into the flask.
9. Insert the mercury seal assembly into the flask.
10. Put the leather belt over the pulley on the stirrer and start the stirrer.
11. Simultaneously start the stopwatch and close the stopcock at point J.

12. Record the temperature and atmospheric pressure at the gas burette. This temperature and pressure is recorded every thirty minutes during the run and at the end of the run. An average of these values is used as the temperature and pressure for the run.

13. At predetermined time intervals, level the leveling bulb, record the elapsed time and the total increase in volume of the gases in the reaction system (gas burette reading). The level of the water in the leveling bulb and gas burette are kept approximately equal at all times during the run.

14. When the run is concluded, stop the reactor stirrer, remove the belt from the pulley, stop the stopwatch, open the stopcock at point J, and remove the mercury seal assembly from the reaction flask. Inspect the hafnium sample surface and note its condition. Rinse the stirrer foot and hafnium sample with distilled water and allow to drain.

15. Remove the acid solution from the reaction flask. Rinse the flask at least twice with distilled water. (A rubber hose connected to a water aspirator is a very convenient means of removing the liquids.)

16. If another run is to be made, repeat steps 2 through 15. If not, shut off the water bath and cover the reaction flask.

The wax-lining in the reaction flask should be examined after each run for holes that would allow acid to contact the glass flask.

Also, the glass joints should be periodically inspected and greased to insure no gas leakage in the system.

Effect of Temperature on the Dissolution Rate of Hafnium in Hydrofluoric Acid and Hydrofluoric-1.00 N Hydrochloric Acid Mixture

The procedure for this part of the experimentation is the same as that given for the measurement of the dissolution rate of hafnium in hydrofluoric acid, this appendix, pages 107 to 110.

Water bath temperatures below the temperature of the cooling water were obtained by adding cracked ice to the bath. The temperature could be controlled very easily within $\pm 0.1^{\circ}C$. It is important to control the level of the water in the water bath so that the immersion of the reaction flask is kept constant.

Effect of Various Additives on the Dissolution Rate of Hafnium in Hydrofluoric Acid

The procedure for this study is divided into two parts: (1) sodium fluoride, potassium fluoride, ammonium fluoride, and lithium sulfate additions and acid mixtures; and (2) noble metal salt, oxidizing agent, mineral acid, and various salt additions.

Procedure for Part 1. The procedure for the runs in which sodium fluorids, etc., were added is the same as that given for the measurement of the dissolution rate of hafnium in hydrofluoric acid, this appendix, pages 107 to 110, except that the following sentence is substituted for the first sentence in Step 3:

3. Place 300 ml of 0.300 N hydrofluoric acid solution containing the desired concentration of the specified salt or acid into the wax-lined reaction flask. The acid is added ...

These additions were made in this manner due to the large amounts of the salts or acids that were necessary to attain some of the desired concentrations.

Procedure for Part 2. The procedure for the additions of noble metal salts, etc., is the same as that given for the measurement of the dissolution rate of hafnium in hydrofluoric acid, this appendix, pages 107 to 110, except the first sentence of Step 3 is substituted as follows and the following steps are added after Step 13:

3. Place 300 ml of 0.300 N hydrofluoric acid in the wax-lined reaction flask. The acid is added ...

13. ... during the run.

13a. Stop the stopwatch at the time at which it is desired to make the addition (normally after a sufficient time has elapsed so that the rate is constant).

13b. Record the elapsed time and the burette reading.

13c. Leaving the leveling bulb in the position at which the reading was taken in Step 13b, immediately open the stopcock at point J and remove the fitting containing the stopcock from the neck of the flask.

13d. Introduce the additive into the acid solution through the open neck of the flask.

13e. Replace the fitting in the neck of the flask.

13f. Simultaneously close the stopcock at J and start the stopwatch.

13g. Continue taking readings in the same manner as before the addition.

14. When the run ...

Steps 13a through 13g should be performed as rapidly as possible. The use of a funnel in Step 13d will prevent the additive from contacting the greased surface of the ground-glass neck of the flask.

Measurement of the Difference Effect on Hafnium in Hydrofluoric-Hydrochloric Acid Mixture

The procedure for this study follows as a step-by-step operation procedure. Refer to Figure 2, page 11, for the nomenclature pertaining to the apparatus. Reference to the data in Appendix D, pages 193 to 199, may also help to clarify the sequence of some of the steps.

1. Start the constant temperature bath by (a) turning on the cooling water and the water bath stirrer, (b) plugging the extension cord from the relay switch into a 115 volt ac source (this is the current source for the heater), and (c) connecting leads from the relay switch to the six-volt battery (this activates the thermoregulator). The thermoregulator is set to maintain the water bath temperature at 25 ± 0.1°C.

2. Disconnect the hafnium and platinized-platinum electrode leads from the ammeter circuit and remove the electrode assembly from the flask. This assembly consists of a female ground-glass fitting for the flask that is sealed at the top with a rubber stopper which holds two glass tubes (electrode holders) in place. The wire leads from the electrodes are threaded through the glass tubes. The electrodes are fastened to the bottom of the holders with wax which serves both to hold the electrodes in place and to seal the tubes.
3. Place 300 ml of hydrofluoric-1.00 N hydrochloric acid mixture of the desired concentration in the wax-lined reaction flask. Cover the flask, start the reactor stirrer, and wait about two hours before starting the run to bring the system to bath temperature. The stirrer rotates at 200 rpm.
4. Mount a hafnium electrode with a freshly prepared surface on the electrode holder and fix in place with wax. The platinized-platinum electrode, with a surface area of approximately four cm^2, is mounted so that the distance between it and the hafnium electrode is 0.5 cm. Directions for preparing and mounting the hafnium electrode in lucite and for preparing the hafnium surface previous to a run are given in Appendices F and G, pages 218 to 225.
5. Adjust the leveling bulb to some initial starting point on the gas burette.

6. Open the knife-blade switch in the ammeter circuit.
7. Open the three-way stopcock and vent the reaction flask to the atmosphere.
8. Insert the electrode assembly into the reaction flask and connect into the ammeter circuit. Care should be taken so that the electrodes are always orientated the same direction with respect to the stirrer.
9. Turn the three-way stopcock to connect the gas burette into the reaction system and simultaneously start the stopwatch. Record atmospheric temperature and pressure at the gas burette. This temperature and pressure is recorded every thirty minutes during the run and at the end of the run. An average of these values is used as the temperature and pressure for the run.
10. At some predetermined time increment, record the volume increase of the gases in the reaction system (burette reading), the anodic current flowing in the ammeter circuit (ammeter reading), and the setting on the resistance box. The first two to four readings (until the readings become fairly constant) are taken with no current flowing, ie., infinite resistance (open switch).
11. Immediately after the last reading in Step 10, close the knife-blade switch in the ammeter circuit. Take two consecutive readings (still at the same time interval) and record the burette readings, ammeter readings, and the

setting on the resistance box. The ammeter reading may fluctuate at higher currents, so a median should be recorded in these cases.

12. Continue to take readings in this manner, two readings without current flowing, two readings with current flowing, until the entire anodic current range for this acid concentration has been covered by five or six current increments. The magnitude of the current can be changed by varying the resistance in the ammeter circuit with the variable resistance box. Normally, the first setting on the resistance box should be high (80 to 100 ohms) and the resistance decreased as the run progresses. However, this can be varied at the investigators discretion so that the current increments will be approximately equal. The last two readings of the run are always taken with no current flowing.

13. To conclude the run, stop the reactor stirrer, disconnect the electrode leads from the ammeter circuit, and remove the electrode assembly from the reaction flask. Rinse the electrodes gently with distilled water and leave immersed in distilled water.

14. Remove the acid solution from the reaction flask and rinse the flask twice with distilled water. The liquids are normally sucked out with a water aspirator.

15. If another run is to be made, repeat Steps 1 through 14. If not, shut off the water bath and cover the reaction flask.

The wax-lining in the reaction flask should be examined after each run for holes that would allow acid to contact the glass. The platinized-platinum electrode should be examined periodically and replatinized when necessary.

Measurement of the Dissolution Potentials of Hafnium in Hydrofluoric Acid and Hydrofluoric-Hydrochloric Acid Mixtures

The procedure for this part of the experimentation follows as a step-by-step operation procedure. Refer to Figure 3, page 13, for nomenclature pertaining to the apparatus.

1. Start the constant temperature bath by (a) turning on the cooling water and water bath stirrer, and (b) plugging the extension cord from the relay switch into a 115 volt ac source which both activates the thermoregulator and supplies current for the knife-blade heater. The thermoregulator must be set to maintain the water bath temperature at the level desired for the run.
2. Open the double-throw switch, remove the hafnium electrode and the solution from the wax-lined reaction beaker.
3. Turn the three-way stopcock on the auxiliary salt bridge so that some of the acid in the reservoir flows through the capillary tip into the empty reaction beaker. Allow four or five milliliters of the acid to flow through the tip so that it is completely flushed. Check to see that no air bubbles are trapped in the capillary. Remove acid from the beaker.

4. Place 300 ml of hydrofluoric acid or hydrofluoric-hydrochloric acid mixture in the wax-lined reaction beaker. Allow it to sit for approximately two hours before starting the run to bring the solution to bath temperature.
5. Close the double-throw switch so as to connect the Weston standard cell into the potentiometer circuit. Adjust the potentiometer to the voltage of the standard cell. Vary the resistance in the circuit with the resistance box so that no deflection is shown on the galvanometer when the key switch is briefly tapped shut. Open the double-throw switch.
6. Very quickly, (a) place the hafnium electrode with a freshly prepared surface into the reaction beaker with the hafnium surface almost touching the capillary tip and hold it in place with a clamp attached to a ring stand, (b) connect the electrode to the double-throw switch, (c) close the double-throw switch so as to connect the cell into the potentiometer circuit, (d) turn the three-way stopcock so as to connect the hafnium half-cell to the saturated potassium chloride salt bridge, and (e) simultaneously start the reactor stirrer and stopwatch. The directions for construction of the hafnium electrode and preparation of the hafnium surface previous to a run are given in Appendices F and G, pages 218 to 225.
7. Adjust the potentiometer so that no deflection is shown by the galvanometer when the key switch is briefly tapped shut.

The potentiometer reading and the elapsed time are then immediately recorded.

8. Further readings as described in Step 7 are taken at five minute intervals until it is decided to end the run.
9. When the last reading of the run has been recorded, (a) close the three-way stopcock on the auxiliary salt-bridge, (b) open the double-throw switch, (c) stop the reactor stirrer, and (d) remove the hafnium electrode and disconnect it from the circuit. The electrode should be rinsed with distilled water and a note made on the condition of the metal surface.
10. Remove the acid solution from the reaction beaker, and rinse it twice with distilled water. (The liquids in the beaker are normally sucked out through a rubber hose connected to a water aspirator.)
11. If another run is to be made, repeat Steps 2 through 10. If not, place 300 ml of distilled water in the reaction flask and shut off the water bath.

The wax-lining in the reaction beaker should be examined after each run for holes which would allow acid to contact the glass. Also, the solutions in the 0.1$\frac{1}{4}$ N HF and the saturated potassium chloride salt bridges should be changed periodically to insure against contamination by diffusion.

Effect of Various Additions on the Dissolution Potentials of Hafnium in Hydrofluoric Acid

The procedure for this study is the same as that given for the measurement of the dissolution potentials of hafnium in hydrofluoric acid, this appendix, pages 116 to 118, except that the following steps are added after Step 7:

7. ... are then immediately recorded.

7a. Further readings as described in Step 7 are taken at five minute intervals until a total time of 40 minutes has elapsed. This is to allow the hafnium electrode reaction to reach a steady state.

7b. Immediately after the 40-minute reading has been taken, the additive is put in the reaction beaker and a reading taken.

8. Further readings at five minute ...

A hydrofluoric acid concentration of 0.300 N was used for all the runs in which additions were made.

Effect of Current Density on the Dissolution Potentials of Hafnium in Hydrofluoric Acid

The procedure for this part of the experimentation is the same as that given for the measurement of the dissolution potentials of hafnium in hydrofluoric acid, this appendix, pages 116 to 118, except that the following step is substituted for Step 8:

8. Further readings are taken with the ammeter circuit closed. The time, ammeter reading, and potentiometer reading

are recorded. The current density (ammeter reading) may be changed by varying the resistance in the ammeter circuit with a variable resistance box. The entire anodic current density range that is obtainable should be covered in four or five approximately equal steps. Time is of no particular consequence in these runs except that at least one or two minutes should be allowed between readings to allow the electrode reactions to reach a more or less steady state.

APPENDIX D

TABLE X

Dissolution of Hf Metal at 30°C in 0.301 N HF and 1.00 N HCl Acid Mixture with Different Stirrer Speeds.

	Run No. 1 (0 rpm) T = 24.0°C P = 736.3 mm Hg			Run No. 2 (90 rpm) T = 22.8°C P = 733.2 mm Hg			Run No. 3 (153 rpm) T = 22.8°C P = 733.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
1	1.20	1.20	1.03						
2	2.10	0.90	0.77*	2.00	2.00	1.72*	2.20	2.20	1.89*
3	3.00	0.90	0.77*						
4	3.80	0.80	0.69*	4.00	2.00	1.72*	4.60	2.40	2.07*
5	4.60	0.80	0.69*						
6	5.60	1.00	0.86*	6.00	2.00	1.72*	6.90	2.30	1.98*
7	6.50	0.90	0.77*						
8	7.40	0.90	0.77*	7.90	1.90	1.64	9.30	2.40	2.07*
9	8.30	0.90	0.77*						
10	9.30	1.00	0.86*	9.80	1.90	1.64	11.60	2.30	1.98*
11[a]	10.20	0.90	0.77*						
12[b]	11.10	0.90	0.77	11.60	1.80	1.55	13.90	2.30	1.98*
13	11.80	0.70	0.60						
14	12.70	0.90	0.77	12.90	1.30	1.12	15.80	1.90	1.64
16				14.90	2.00	1.72	18.20	2.40	2.07
18				16.80	1.90	1.64	20.50	2.30	1.98
20				18.70	1.90	1.64	22.80	2.30	1.98
22				20.60	1.90	1.64	25.00	2.20	1.89
24				22.40	1.80	1.55			
Ave. Rate (ml/min)			0.77			0.86			1.00

[a] Added 20 ml of 15%w KI solution to acid solution in Run No. 1.
[b] Added 2.54 gm of NaCl to acid solution in Run No. 2.
[b] Added 1.55 gm of KCl to acid solution in Run No. 3.

TABLE XI

Dissolution of Hf Metal at 30°C in 0.301 N HF and 1.00 N HCl Acid Mixture with Different Stirrer Speeds.

	Run No. 4 (229 rpm) T = 23.5°C P = 735.9 mm Hg			Run No. 5 (269 rpm) T = 22.8°C P = 736.0 mm Hg			Run No. 6 (321 rpm) T = 24.6°C P = 736.7 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	2.80	2.80	2.41*	2.80	2.80	2.42*	3.50	3.50	3.00
4	5.50	2.70	2.32*	5.70	2.90	2.51*	6.90	3.40	2.92
6	8.10	2.60	2.24*	8.50	2.80	2.42*	9.90	3.00	2.57
8	10.80	2.70	2.32*	11.20	2.70	2.33	13.00	3.10	2.66*
10	13.60	2.80	2.41*	14.10	2.90	2.51	16.30	3.30	2.83*
12[a]	16.20	2.60	2.24*	16.90	2.80	2.42	19.40	3.10	2.66*
14	18.90	2.70	2.32	19.60	2.70	2.33	22.40	3.00	2.57
16[b]	21.50	2.60	2.24	22.30	2.70	2.33	25.30	2.90	2.49
17							31.10	5.80	4.97
18	24.10	2.60	2.24	25.10	2.80	2.42	35.40	4.30	3.69
19							39.10	3.70	3.17
20	26.60	2.50	2.15	27.80	2.70	2.33	42.70	3.60	3.09
21							46.00	3.30	2.83
22	29.10	2.50	2.15				49.00	3.00	2.57
23							51.60	2.60	2.23
24	31.60	2.50	2.15				54.00	2.40	2.06
Ave. Rate (ml/min)			1.16			1.23			1.36

[a] Added 3.82 gm of NaBr to acid solution in Run No. 4.
[a] Added 2.26 gm of $NaNO_3$ to acid solution in Run No. 5.
[b] Added 2.22 gm of $NaBiO_3$ to acid solution in Run No. 6.

TABLE XII

Dissolution of Hf Metal at 30°C in 0.301 N HF and 1.00 N HCl Acid Mixture with Different Stirrer Speeds.

	Run No. 7 (396 rpm) T = 23.4°C P = 736.4 mm Hg			Run No. 8 (540 rpm) T = 23.5°C P = 737.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	3.50	3.50	3.02*	3.80	3.80	3.28
4	7.00	3.50	3.02*	8.00	4.20	3.63*
6	10.60	3.60	3.10*	12.10	4.10	3.54*
8	14.10	3.50	3.02*	16.10	4.00	3.45*
10	17.50	3.40	2.93	20.10	4.00	3.45*
12[a]	21.90	3.40	2.93	24.10	4.00	3.45*
14	24.20	2.30	1.98	27.40	3.30	2.85
16	27.60	3.40	2.93	31.00	3.60	3.11
18	31.80	3.20	2.76	34.70	3.60	3.11
20	34.20	2.40	2.07	38.30	3.60	3.11
22	37.40	3.20	2.76	41.80	3.50	3.02
24	40.70	3.30	2.85			
26	44.00	3.30	2.85			
Ave. Rate (ml/min)			1.52			1.75

[a] Added 1.91 gm of Sodium Citrate to acid solution in Run No. 7.

[a] Added 20 ml of 0.1 N $K_2Cr_2O_7$ solution to acid solution in Run No. 8.

TABLE XIII

Dissolution of Hf Metal in 0.050 N Hydrofluoric Acid at 25°C.

	Run No. 1 T = 29.0°C P = 736.6 mm Hg			Run No. 2 T = 29.2°C P = 736.3 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	0.40	0.40	0.335	0.40	0.40	0.334
20	1.20	0.80	0.669	1.20	0.80	0.668
30	2.10	0.90	0.753	2.40	1.20	1.002*
40	3.40	1.30	1.087*	3.40	1.00	0.835*
50	4.50	1.10	0.920*	4.70	1.30	1.086*
60	5.60	1.10	0.920*	5.80	1.10	0.918*
Ave. Rate (ml/min)			0.0976			0.0960

* Values averaged to get average maximum rate.

TABLE XIV

Dissolution of Hf Metal in 0.100 N Hydrofluoric Acid at 25°C.

	Run No. 1 T = 28.1°C P = 732.8 mm Hg			Run No. 2 T = 30.2°C P = 732.8 mm Hg			Run No. 3 T = 29.0°C P = 733.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
10	1.60	1.60	1.339	1.20	1.20	0.992	1.20	1.20	1.000
20	4.00	2.40	2.008	3.80	2.60	2.147*	3.80	2.60	2.166*
30	6.50	2.50	2.092*	6.40	2.60	2.147*	6.50	2.70	2.249*
40	9.00	2.50	2.092*	8.90	2.50	2.065*	9.10	2.60	2.166*
50	11.30	2.30	1.925	11.20	2.30	1.900	11.60	2.50	2.083*
60							14.20	2.60	2.166*
Ave. Rate (ml/min)			0.209			0.212			0.217

* Values averaged to get average maximum rate.

TABLE XV

Dissolution of Hf Metal in 0.500 N Hydrofluoric Acid at 25°C.

Run No. 1
T = 29.8°C
P = 733.0 mm Hg

Time	Vol	dV	dV STP
min	ml	ml	ml
0	0.00	---	---
5	5.60	5.60	4.637
10	12.40	6.80	5.631*
15	19.00	6.60	5.465*
20	25.60	6.60	5.465*
25	32.30	6.70	5.548*
30	38.80	6.50	5.383*
Ave. Rate (ml/min)			1.10

* Values averaged to get average maximum rate.

TABLE XVI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 10°C.

	Run No. 1 T = 31.7°C P = 734.9 mm Hg			Run No. 2 T = 31.6°C P = 738.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
10	0.20	0.20	0.164	1.00	1.00	0.826
20	0.90	0.70	0.575	1.60	0.60	0.495
30	2.30	1.40	1.149*	2.50	0.90	0.743
40	3.60	1.30	1.067*	3.80	1.30	1.073*
50	4.90	1.30	1.067*	5.20	1.40	1.156*
60	6.10	1.20	0.985*	6.20	1.00	0.826*
70	7.20	1.10	0.903*	7.50	1.30	1.073*
80	8.60	1.40	1.149*	8.70	1.20	0.991*
90				9.80	1.10	0.908*
Ave. Rate (ml/min)			0.105			0.100

* Values averaged to get average maximum rate.

TABLE XVII

Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 10°C.

	Run No. 1 T = 28.5°C P = 740.2 mm Hg			Run No. 2 T = 26.9°C P = 739.7 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	0.80	0.80	0.675	0.70	0.70	0.595
20	2.30	1.50	1.265	2.40	1.70	1.446
30	4.50	2.20	1.855	4.40	2.00	1.701
40	7.10	2.60	2.192*	6.70	2.30	1.956*
50	9.60	2.50	2.108*	9.00	2.30	1.956*
60	12.10	2.50	2.108*	11.30	2.30	1.956*
70	14.60	2.50	2.108*	13.60	2.30	1.956*
80	17.00	2.40	2.024*	15.90	2.30	1.956*
90	19.50	2.50	2.108*	18.20	2.30	1.956*
100	21.80	2.30	1.939			
Ave. Rate (ml/min)			0.211			0.196

* Values averaged to get average maximum rate.

TABLE XVIII

Dissolution of Hf Metal in 0.300 N HF and 1.00 N HCl Acid Mixture at 10°C.

	Run No. 1 T = 32.7°C P = 737.9 mm Hg			Run No. 2 T = 33.0°C P = 737.5 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
5	1.10	1.10	0.901	1.00	1.00	0.817
10	4.10	3.00	2.457	4.20	3.20	2.614
15	7.30	3.20	2.621	8.00	3.80	3.105*
20	10.80	3.50	2.867*	11.60	3.60	2.941*
25	14.20	3.40	2.785*	15.30	3.70	3.023*
30	17.80	3.60	2.948*	18.80	3.50	2.860*
35	21.20	3.40	2.785*	22.30	3.50	2.860*
40	24.60	3.40	2.785*	25.90	3.60	2.941*
45	27.80	3.20	2.621	29.00	3.10	2.533*
50	31.10	3.30	2.703	32.70	3.70	3.023*
55	34.40	3.30	2.703	35.90	3.20	2.614*
60				39.60	3.70	3.023*
Ave. Rate (ml/min)			0.567			0.578

* Values averaged to get average maximum rate.

TABLE XIX

Dissolution of Hf Metal in 0.503 N HF and 1.00 N HCl Acid Mixture at 10°C.

	Run No. 1 T = 29.7°C P = 737.4 mm Hg			Run No. 2 T = 30.2°C P = 737.1 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
3	1.40	1.40	1.167	1.70	1.70	1.413
6	4.50	3.10	2.585	4.70	3.00	2.493
9	8.20	3.70	3.085*	8.40	3.70	3.074*
12	12.00	3.80	3.168*	12.10	3.70	3.074*
15	15.80	3.80	3.168*	15.70	3.60	2.991*
18	19.40	3.60	3.002*	19.10	3.40	2.825*
21	23.00	3.60	3.002*	22.90	3.80	3.157*
24	26.60	3.60	3.002*	26.60	3.70	3.074*
27	30.20	3.60	3.002*	30.40	3.80	3.157*
Ave. Rate (ml/min)			1.020			1.017

* Values averaged to get average maximum rate.

TABLE XX

Dissolution of Hf Metal in 1.00 N HF and 1.00 N HCl Acid Mixture at 10°C.

	Run No. 1 T = 29.8°C P = 737.3 mm Hg			Run No. 2 T = 30.5°C P = 736.7 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	0.80	0.80	0.666	2.30	2.30	1.907
4	3.70	2.90	2.416	5.50	3.20	2.653
6	7.70	4.00	3.332	9.50	4.00	3.316
8	12.70	5.00	4.166*	14.30	4.80	3.980
10	17.70	5.00	4.166*	19.50	5.20	4.311*
12	23.00	5.30	4.415*	24.60	5.10	4.228*
14	28.10	5.10	4.249*	30.00	5.40	4.477*
16	33.10	5.00	4.166*	35.40	5.40	4.477*
18	38.00	4.90	4.082*	40.60	5.20	4.311*
20	43.20	5.20	4.332*			
22	48.20	5.00	4.166*			
Ave. Rate (ml/min)			2.109			2.180

* Values averaged to get average maximum rate.

TABLE XXI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 20°C.

	Run No. 1 T = 26.2°C P = 735.7 mm Hg			Run No. 2 T = 27.3°C P = 734.8 mm Hg			Run No. 3 T = 30.2°C P = 732.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
10	0.40	0.40	0.340	1.00	1.00	0.829	0.00	0.00	0.000
20	1.50	1.10	0.934	3.10	2.10	1.741*	1.40	1.40	1.156*
30	2.80	1.30	1.104*	5.00	1.90	1.575*	3.40	2.00	1.651*
40	4.20	1.40	1.189*	7.00	2.00	1.658*	5.10	1.70	1.403*
50	5.70	1.50	1.274*	9.20	2.20	1.824*	6.50	1.40	1.156*
60	7.10	1.40	1.189*	11.20	2.00	1.658*	8.30	1.80	1.486*
70	8.60	1.50	1.274*	13.30	2.10	1.741*	9.80	1.50	1.238*
80	10.20	1.60	1.358*	15.40	2.10	1.741*			
90	11.80	1.60	1.358*	17.20	1.80	1.492*			
100				19.20	2.00	1.658*			
110				21.20	2.00	1.658*			
Ave. Rate (ml/min)			0.125			0.168			0.135

* Values averaged to get average maximum rate.

TABLE XXI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 20°C. (Continued)

	Run No. 4 T = 29.8°C P = 736.1 mm Hg			Run No. 5 T = 30.8°C P = 735.3 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	1.20	1.20	0.998	0.40	0.40	0.330
20	2.70	1.50	1.248*	1.80	1.40	1.156*
30	4.20	1.50	1.248*	3.40	1.60	1.321*
40	5.80	1.60	1.331*	5.20	1.80	1.486*
50	7.60	1.80	1.497*	6.80	1.60	1.321*
60	9.10	1.50	1.248*	8.40	1.60	1.321*
70	10.50	1.40	1.164*	10.00	1.60	1.321*
80	12.30	1.80	1.497*	11.40	1.40	1.156*
90				12.90	1.50	1.239*
100				14.40	1.50	1.239*
110				15.90	1.50	1.239*
120				17.40	1.50	1.239*
Ave. Rate (ml/min)			0.132			0.128

* Values averaged to get average maximum rate.

TABLE XXII

Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 20°C.

	Run No. 1 T = 28.6°C P = 737.0 mm Hg			Run No. 2 T = 30.1°C P = 739.0 mm Hg			Run No. 3 T = 30.8°C P = 737.7 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
10	2.20	2.20	1.845	1.50	1.50	1.251	1.60	1.60	1.326
20	5.20	3.00	2.516	4.40	2.90	2.418	4.50	2.90	2.403
30	8.40	3.20	2.684	7.50	3.10	2.584*	7.40	2.90	2.403
40	11.80	3.40	2.852*	10.70	3.20	2.668*	10.60	3.20	2.652*
50	15.20	3.40	2.852*	13.80	3.10	2.584*	13.60	3.00	2.486*
60	18.50	3.30	2.768	16.50	2.70	2.251	16.60	3.00	2.486*
70	21.60	3.10	2.600	19.80	3.30	2.751*	19.50	2.90	2.403
80	24.60	3.00	2.516	22.80	3.00	2.501*	22.50	3.00	2.486
90				26.00	3.20	2.668*	25.30	2.80	2.320
Ave. Rate (ml/min)			0.285			0.262			0.254

* Values averaged to get average maximum rate.

TABLE XXIII

Dissolution of Hf Metal in 0.303 N HF and 1.00 N HCl Acid Mixture at 20°C.

	Run No. 1 T = 34.5°C P = 738.6 mm Hg			Run No. 2 T = 32.9°C P = 739.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
5	3.60	3.60	2.917	3.90	3.90	3.198
10	8.60	5.00	4.051*	8.70	4.80	3.936*
15	14.00	5.40	4.375*	13.90	5.20	4.265*
20	19.20	5.20	4.213*	19.20	5.30	4.347*
25	24.40	5.20	4.213*	24.00	4.80	3.936*
30	29.50	5.10	4.132*	29.10	5.10	4.183*
35				34.00	4.90	4.108*
Ave. Rate (ml/min)			0.839			0.823

* Values averaged to get average maximum rate.

TABLE XXIV

Dissolution of Hf Metal in 0.503 N HF and 1.00 N HCl Acid Mixture at 20°C.

	Run No. 1 T = 32.7°C P = 736.9 mm Hg			Run No. 2 T = 33.0°C P = 736.5 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
3	3.80	3.80	3.108	3.80	3.80	3.100
6	9.00	5.20	4.253*	8.70	4.90	3.998*
9	14.20	5.20	4.253*	13.80	5.10	4.161*
12	19.60	5.40	4.416*	18.80	5.00	4.080*
15	24.80	5.20	4.253*	23.80	5.00	4.080*
18	29.90	5.10	4.171*	28.30	4.50	3.672*
21	35.20	5.30	4.334*	33.40	5.10	4.161*
24	40.40	5.20	4.253*			
27	45.60	5.20	4.253*			
Ave. Rate (ml/min)			1.424			1.342

* Values averaged to get average maximum rate.

TABLE XXV

Dissolution of Hf Metal in 1.00 N HF and 1.00 N HCl Acid Mixture at 20°C.

	Run No. 1 T = 31.0°C P = 735.2 mm Hg			Run No. 2 T = 31.3°C P = 734.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	2.00	2.00	1.649	2.20	2.20	1.810
2	4.10	2.10	1.732	4.70	2.50	2.057
3	6.60	2.50	2.062	7.30	2.60	2.139
4	9.40	2.80	2.309	10.30	3.00	2.468
5	12.40	3.00	2.474	13.40	3.10	2.550
6	15.80	3.40	2.804*	16.60	3.20	2.633*
7	19.20	3.40	2.804*	19.80	3.20	2.633*
8	22.70	3.50	2.886*	23.10	3.30	2.715*
9	26.30	3.60	2.969*	26.60	3.50	2.879*
10	29.90	3.60	2.969*	30.20	3.60	2.962*
11	33.50	3.60	2.969*	33.70	3.50	2.879*
12	37.20	3.70	3.051*	37.20	3.50	2.879*
13	40.80	3.60	2.969*	40.60	3.40	2.797*
14	44.50	3.70	3.051*	44.30	3.70	3.044*
15	48.10	3.60	2.969*	47.80	3.50	2.879*
16	51.80	3.70	3.051*			
Ave. Rate (ml/min)			2.954			2.830

* Values averaged to get average maximum rate.

TABLE XXVI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 30°C.

	Run No. 1 T = 28.4°C P = 735.8 mm Hg			Run No. 2 T = 29.5°C P = 735.3 mm Hg			Run No. 3 T = 29.6°C P = 735.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
10	1.60	1.60	1.341	1.80	1.80	1.498	1.50	1.50	1.248
20	3.30	1.70	1.425*	3.90	2.10	1.748*	3.60	2.10	1.748*
30	5.00	1.70	1.425*	5.90	2.00	1.665*	5.70	2.10	1.748*
40	7.10	2.10	1.761*	7.90	2.00	1.665*	7.80	2.10	1.748*
50	8.80	1.70	1.425*	9.90	2.00	1.665*	9.80	2.00	1.665*
60	10.70	1.90	1.593*	11.80	1.90	1.581*	11.80	2.00	1.665*
70	12.60	1.90	1.593*	13.70	1.90	1.581*			
80	14.70	2.10	1.761*	15.70	2.00	1.665*			
90				17.60	1.90	1.581*			
Ave. Rate (ml/min)			0.157			0.164			0.172

* Values averaged to get average maximum rate.

TABLE XXVII

Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 30°C.

	Run No. 1 T = 30.9°C P = 738.6 mm Hg			Run No. 2 T = 31.6°C P = 738.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	3.80	3.80	3.151	3.80	3.80	3.135
20	8.00	4.20	3.483*	8.40	4.60	3.795*
30	12.20	4.20	3.483*	12.80	4.40	3.630*
40	16.30	4.10	3.400	17.10	4.30	3.548
50	20.30	4.00	3.317	21.30	4.20	3.465
60	24.10	3.80	3.151	25.30	4.00	3.300
70	27.70	3.60	2.985			
Ave. Rate (ml/min)			0.348			0.371

* Values averaged to get average maximum rate.

TABLE XXVIII

Dissolution of Hf Metal in 0.303 N HF and 1.00 N HCl Acid Mixture at 30°C.

	Run No. 1 T = 34.5°C P = 738.0 mm Hg			Run No. 2 T = 35.0°C P = 736.7 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
5	6.00	6.00	4.863	6.00	6.00	4.831
10	12.80	6.80	5.511*	12.70	6.70	5.395*
15	19.80	7.00	5.674*	19.50	6.80	5.475*
20	26.30	6.50	5.268*	26.00	6.50	5.234*
25	32.80	6.50	5.268*	32.60	6.60	5.314*
30	39.60	6.80	5.511*	39.20	6.60	5.314*
35	46.20	6.60	5.349*	45.70	6.50	5.234*
Ave. Rate (ml/min)			1.086			1.066

* Values averaged to get average maximum rate.

TABLE XXIX

Dissolution of Hf Metal in 0.503 N HF and 1.00 N HCl Acid Mixture at 30°C.

	Run No. 1 T = 30.4°C P = 739.0 mm Hg			Run No. 2 T = 31.5°C P = 738.5 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	3.80	3.80	3.162	3.40	3.40	2.807
4	8.10	4.30	3.578*	7.70	4.30	3.550*
6	12.60	4.50	3.745*	12.10	4.40	3.633*
8	17.20	4.60	3.828*	16.60	4.50	3.715*
10	21.60	4.40	3.662*	21.00	4.40	3.633*
12	25.90	4.30	3.578*	25.30	4.30	3.550*
14	30.40	4.50	3.745*	29.60	4.30	3.550*
16	34.90	4.50	3.745*	33.90	4.30	3.550*
18	39.20	4.30	3.578*	38.20	4.30	3.550*
20	43.60	4.40	3.662*	42.40	4.20	3.468*
Ave. Rate (ml/min)			1.840			1.789

* Values averaged to get average maximum rate.

TABLE XXX

Dissolution of Hf Metal in 1.00 N HF and 1.00 N HCl Acid Mixture at 30°C.

	Run No. 1 T = 31.5°C P = 732.0 mm Hg			Run No. 2 T = 30.5°C P = 731.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	3.50	3.50	2.864	3.20	3.20	2.631
2	7.40	3.90	3.191	7.40	4.20	3.454*
3	11.50	4.10	3.355*	11.70	4.30	3.536*
4	15.60	4.10	3.355*	16.20	4.50	3.700*
5	19.80	4.20	3.437*	20.80	4.60	3.783*
6	24.00	4.20	3.437*	25.20	4.40	3.618*
7	28.20	4.20	3.437*	29.70	4.50	3.700*
8	32.40	4.20	3.437*	34.20	4.50	3.700*
Ave. Rate (ml/min)			3.410			3.641

* Values averaged to get average maximum rate.

TABLE XXXI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 40°C.

	Run No. 1 T = 30.0°C P = 736.5 mm Hg			Run No. 2 T = 30.8°C P = 736.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
10	2.90	2.90	2.411*	3.00	3.00	2.480*
20	5.50	2.60	2.161*	5.50	2.50	2.067*
30	8.00	2.50	2.078*	8.00	2.50	2.067*
40	10.60	2.60	2.161*	10.70	2.70	2.232*
50	13.10	2.50	2.078*	13.00	2.30	1.901*
60	15.30	2.20	1.829	15.40	2.40	1.984*
70				18.10	2.60	2.149*
80				20.70	2.60	2.149*
Ave. Rate (ml/min)			0.218			0.213

* Values averaged to get average maximum rate.

TABLE XXXII

Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 40°C.

	Run No. 1 T = 29.2°C P = 740.6 mm Hg			Run No. 2 T = 31.0°C P = 740.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	5.30	5.30	4.452	5.00	5.00	4.153
20	10.80	5.50	4.621*	10.50	5.50	4.568*
30	16.40	5.60	4.705*	15.80	5.30	4.402*
40	21.50	5.10	4.285	20.90	5.10	4.236
50	26.60	5.10	4.285	25.80	4.90	4.070
60	31.60	5.00	4.201	30.60	4.80	3.987
70	36.40	4.80	4.032			
Ave. Rate (ml/min)			0.466			0.449

* Values averaged to get average maximum rate.

TABLE XXXIII

Dissolution of Hf Metal in 0.303 N HF and 1.00 N HCl Acid Mixture at 40°C.

	Run No. 1 T = 29.2°C P = 736.6 mm Hg			Run No. 2 T = 31.3°C P = 735.9 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
3	5.30	5.30	4.427*	4.80	4.80	3.955
6	10.50	5.20	4.344*	10.00	5.20	4.285*
9	15.90	5.40	4.511*	15.30	5.30	4.376*
12	21.20	5.30	4.427*	20.40	5.10	4.202*
15	26.00	4.80	4.009	25.60	5.20	4.285*
18	31.00	5.00	4.177	30.60	5.00	4.120*
21				35.80	5.20	4.285*
Ave. Rate (ml/min)			1.476			1.419

* Values averaged to get average maximum rate.

TABLE XXXIV

Dissolution of Hf Metal in 0.503 N HF and 1.00 N HCl Acid Mixture at 40°C.

	Run No. 1 T = 34.4°C P = 737.5 mm Hg			Run No. 2 T = 33.3°C P = 737.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	2.70	2.70	2.186	3.20	3.20	2.607*
2	5.60	2.90	2.348	6.20	3.00	2.444*
3	8.70	3.10	2.509*	9.40	3.20	2.607*
4	11.80	3.10	2.509*	12.40	3.00	2.444*
5	15.10	3.30	2.671*	15.40	3.00	2.444*
6	18.00	2.90	2.348	18.50	3.10	2.526*
7	21.10	3.10	2.509	21.40	2.90	2.363
8	24.10	3.00	2.429	24.30	2.90	2.363
9	27.10	3.00	2.429	27.20	2.90	2.363
10	30.20	3.10	2.509	30.20	3.00	2.444
11	33.30	3.10	2.509	33.10	2.90	2.363
12	36.30	3.00	2.429	36.00	2.90	2.363
Ave. Rate (ml/min)			2.563			2.512

* Values averaged to get average maximum rate.

TABLE XXXV

Dissolution of Hf Metal in 1.00 N HF and 1.00 N HCl Acid Mixture at 40°C.

	Run No. 1 T = 30.3°C P = 730.3 mm Hg			Run No. 2 T = 28.6°C P = 730.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
1	5.10	5.10	4.194	5.00	5.00	4.155
2	11.10	6.00	4.934*	10.60	5.60	4.654*
3	17.40	6.30	5.181*	16.50	5.90	4.903*
4	23.60	6.20	5.099*	22.40	5.90	4.903*
5	30.00	6.40	5.263*	28.40	6.00	4.986*
6	36.30	6.30	5.181*	34.40	6.00	4.986*
7	42.80	6.50	5.346	40.40	6.00	4.986*
8	49.30	6.50	5.346	46.40	6.00	4.986*
Ave. Rate (ml/min)			5.126			4.902

* Values averaged to get average maximum rate.

TABLE XXXVI

Dissolution of Hf Metal in 0.050 N HF and 1.00 N HCl Acid Mixture at 50°C.

	Run No. 1 T = 28.3°C P = 735.7 mm Hg			Run No. 2 T = 29.6°C P = 734.5 mm Hg			Run No. 3 T = 29.3°C P = 734.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
10	5.00	5.00	4.194*	3.60	3.60	2.992*	4.10	4.10	3.411*
20	8.00	3.00	2.516*	7.20	3.60	2.992*	7.50	3.40	2.829*
30	11.00	3.00	2.516*	10.00	2.80	2.327*	10.80	3.30	2.746*
40	14.30	3.30	2.768*	13.30	3.30	2.742*	13.90	3.10	2.579*
50	17.10	2.80	2.349*	16.40	3.10	2.576*	17.20	3.30	2.746*
60	20.00	2.90	2.433	19.20	2.80	2.327	20.30	3.10	2.579
70							23.30	3.00	2.496
Ave. Rate (ml/min)			0.300			0.273			0.286

* Values averaged to get average maximum rate.

TABLE XXXVII

Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 50°C.

	Run No. 1 T = 29.6°C P = 738.1 mm Hg			Run No. 2 T = 31.4°C P = 736.6 mm Hg			Run No. 3 T = 31.4°C P = 735.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
10	7.30	7.30	6.097*	7.20	7.20	5.935*	7.00	7.00	5.763*
20	13.90	6.60	5.512	13.70	6.50	5.358	13.80	6.80	5.598
30	19.80	5.90	4.928	20.00	6.30	5.193	20.30	6.50	5.351
40	26.40	6.60	5.512	26.20	6.20	5.111	26.80	6.50	5.351
50	32.30	5.90	4.928	32.40	6.20	5.111	33.00	6.20	5.104
60				38.00	5.60	4.616	39.10	6.10	5.022
70				43.80	5.80	4.781	44.60	5.50	4.528
80				49.60	5.80	4.781	50.40	5.80	4.775
Ave. Rate (ml/min)			0.610			0.594			0.576

* Values averaged to get average maximum rate.

TABLE XXXVIII

Dissolution of Hf Metal in 0.303 N HF and 1.00 N HCl Acid Mixture at 50°C.

	Run No. 1 T = 32.2°C P = 735.2 mm Hg			Run No. 2 T = 31.2°C P = 738.3 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	4.50	4.50	3.683*	4.60	4.60	3.806*
4	9.00	4.50	3.683*	8.60	4.00	3.309*
6	13.50	4.50	3.683*	12.90	4.30	3.557*
8	17.80	4.30	3.520	17.20	4.30	3.557*
10	22.00	4.20	3.438	21.40	4.20	3.475
12	26.30	4.30	3.520	25.50	4.10	3.392
14	30.50	4.20	3.438	29.80	4.30	3.557
16	34.80	4.30	3.520	34.00	4.20	3.475
18				38.10	4.10	3.392
Ave. Rate (ml/min)			1.842			1.778

* Values averaged to get average maximum rate.

TABLE XXXIX

Dissolution of Hf Metal in 0.503 N HF and 1.00 N HCl Acid Mixture at 50°C.

	Run No. 1 T = 32.2°C P = 737.3 mm Hg			Run No. 2 T = 31.7°C P = 738.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	3.90	3.90	3.202*	3.80	3.80	3.134*
2	7.70	3.80	3.120*	7.50	3.70	3.052*
3	11.60	3.90	3.202*	11.20	3.70	3.052*
4	15.50	3.90	3.202*	15.00	3.80	3.134*
5	19.40	3.90	3.202*	18.60	3.60	2.969*
6	22.40	3.00	2.463	22.60	4.00	3.299*
7	26.40	4.00	3.284	26.00	3.40	2.804
8	30.40	4.00	3.284	29.50	3.50	2.887
9	34.00	3.60	2.956	33.20	3.70	3.052
10	37.70	3.70	3.038	36.80	3.60	2.969
11	41.20	3.50	2.874	40.70	3.90	3.217
12				44.40	3.70	3.052
Ave. Rate (ml/min)			3.186			3.107

* Values averaged to get average maximum rate.

TABLE XL

Dissolution of Hf Metal in 1.00 N HF and 1.00 N HCl Acid Mixture at 50°C.

	Run No. 1 T = 29.8°C P = 729.4 mm Hg			Run No. 2 T = 30.0°C P = 729.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
1	7.80	7.80	6.426	8.00	8.00	6.583
2	16.00	8.20	6.756*	16.60	8.60	7.077*
3	24.30	8.30	6.838*	25.20	8.60	7.077*
4	32.50	8.20	6.756*	34.30	9.10	7.488
5	41.40	8.90	7.333	43.20	8.90	7.324
6	49.80	8.40	6.921	52.20	9.00	7.406
7	58.70	8.90	7.333	61.80	9.60	7.900
8	67.30	8.60	7.086	70.80	9.00	7.406
9				79.80	9.00	7.406
Ave. Rate (ml/min)			6.783			7.077

* Values averaged to get average maximum rate.

TABLE XLI

Dissolution of Hf Metal in 0.100 N Hydrofluoric Acid at 5°C.

	Run No. 1 T = 31.2°C P = 735.7 mm Hg			Run No. 2 T = 32.6°C P = 734.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	--	--
10	0.00	0.00	0.000	0.00	0.00	0.000
20	0.00	0.00	0.000	0.00	0.00	0.000
30	0.60	0.60	0.495	0.60	0.60	0.489
40	1.40	0.80	0.659	1.30	0.70	0.571
50	2.60	1.20	0.989*	2.40	1.10	0.897*
60	3.80	1.20	0.989*	5.40	3.00	2.446
70	5.20	1.40	1.154*	7.00	1.60	1.304*
80	7.50	2.30	1.896	8.40	1.40	1.141*
90	9.00	1.50	1.236*	9.70	1.30	1.060*
100	10.10	1.10	0.907*	10.90	1.20	0.978*
110	11.60	1.50	1.236*	12.10	1.20	0.978*
120	12.70	1.10	0.907*	13.50	1.40	1.141*
130	14.00	1.30	1.071*	14.60	1.10	0.897*
140	16.10	2.10	1.731			
150	19.40	1.30	1.071*			
Ave. Rate (ml/min)			0.106			0.106

* Values averaged to get average maximum rate.

TABLE XLII

Dissolution of Hf Metal in 0.100 N Hydrofluoric Acid at 15°C.

	Run No. 1 T = 30.0°C P = 738.0 mm Hg			Run No. 2 T = 32.3°C P = 737.3 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
10	0.00	0.00	0.000	0.20	0.20	0.164
20	1.20	1.20	1.000	1.40	1.20	0.985
30	3.00	1.80	1.500*	3.30	1.90	1.559*
40	4.80	1.80	1.500*	5.50	2.20	1.805
50	6.50	1.70	1.416*	7.40	1.90	1.559*
60	9.00	2.50	2.083	9.40	2.00	1.640*
70	10.70	1.70	1.416*	11.90	2.50	2.052
80	12.50	1.80	1.500*	13.80	1.90	1.559*
90	14.70	2.20	1.833	15.60	1.60	1.313*
100	16.50	1.80	1.500*	17.60	2.00	1.641*
110	18.20	1.70	1.416*	19.10	1.50	1.231*
120	19.80	1.60	1.333	20.90	1.80	1.477*
130				22.90	2.00	1.641*
140				24.60	1.50	1.231*
150				26.40	1.80	1.477*
Ave. Rate (ml/min)			0.146			0.148

* Values averaged to get average maximum rate.

TABLE XLIII

Dissolution of Hf Metal in 0.100 N Hydrofluoric Acid at 35°C.

	Run No. 1 T = 30.1°C P = 734.5 mm Hg			Run No. 2 T = 28.0°C P = 733.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
10	2.85	2.85	2.361	3.20	3.20	2.680
20	6.40	3.55	2.941*	6.60	3.40	2.848*
30	9.50	3.10	2.568*	9.85	3.25	2.722*
40	12.80	3.30	2.734*	12.90	3.15	2.638*
50	15.90	3.10	2.568	16.00	3.10	2.597
60	19.00	3.10	2.568	19.10	3.10	2.597
Ave. Rate (ml/min)			0.275			0.274

* Values averaged to get average maximum rate.

TABLE XLIV

Dissolution of Hf Metal in 0.100 N Hydrofluoric Acid at 45°C.

	Run No. 1 T = 30.0°C P = 733.1 mm Hg			Run No. 2 T = 30.6°C P = 732.9 mm Hg			Run No. 3 T = 28.0°C P = 736.4 mm Hg			Run No. 4 T = 29.0°C P = 735.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--	0.00	--	--
10	4.80	4.80	3.971*	5.70	5.70	4.697*	5.20	5.20	4.374*	5.20	5.20	4.339*
20	8.60	3.80	3.144*	10.20	4.50	3.708*	9.50	4.30	3.617*	9.40	4.20	3.505*
30	12.20	3.60	2.978*	14.20	4.00	3.296*	13.60	4.10	3.449*	13.60	4.20	3.505*
40	16.20	4.00	3.309*	18.00	3.80	3.131*	17.60	4.00	3.365*	17.20	3.60	3.004*
50	20.00	3.80	3.144	22.20	4.20	3.461*	21.30	3.70	3.112	21.40	4.20	3.505*
60	23.60	3.60	2.978	26.20	4.00	3.296	25.10	3.80	3.197	24.80	3.40	2.837
70				29.60	3.40	2.802				28.40	3.60	3.004
80				33.60	4.00	3.296				31.80	3.40	2.837
90										35.30	3.50	2.921
100										38.80	3.50	2.921
110										42.40	3.60	3.004
120										45.80	3.40	2.837
130										49.20	3.40	2.837
140										52.10	2.90	2.420
Ave. Rate (ml/min)			0.335			0.366			0.370			0.357

* Values averaged to get average maximum rate.

TABLE XLV

Dissolution of Hf Metal in 0.301 N HF Acid at 30°C with NaF Addition.

	Run No. 1 0.050 M NaF T = 27.5°C P = 737.2 mm Hg			Run No. 2 0.075 M NaF T = 28.8°C P = 736.4 mm Hg			Run No. 3 0.100 M NaF T = 23.5°C P = 736.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
2	1.70	1.70	1.44	1.60	1.60	1.34	2.00	2.00	1.73
4	3.30	1.60	1.35	3.70	2.10	1.76*	4.10	2.10	1.81*
6	5.50	2.20	1.86*	5.70	2.00	1.67*	6.30	2.20	1.90*
8	7.50	2.00	1.69*	7.60	1.90	1.59*	8.50	2.20	1.90*
10	9.60	2.10	1.77*	9.70	2.10	1.76*	10.70	2.20	1.90*
12	11.60	2.00	1.69*	11.80	2.10	1.76*	12.80	2.10	1.81*
14	13.50	1.90	1.60*	14.00	2.20	1.84*	14.80	2.00	1.73
16	15.50	2.00	1.69*	16.00	2.00	1.67*	16.90	2.10	1.81
18	17.40	1.90	1.60*	18.10	2.10	1.76*	19.00	2.10	1.81
20	19.50	2.10	1.77*	20.00	1.90	1.59	21.10	2.10	1.81
22	21.30	1.80	1.52	21.90	1.90	1.59	23.20	2.10	1.81
24	23.10	1.80	1.52	24.00	2.10	1.76	25.20	2.00	1.73
26	25.10	2.00	1.69	26.00	2.00	1.67	27.30	2.10	1.81
Ave. Rate (ml/min)			0.85			0.86			0.93

* Values averaged to get average maximum rate.

TABLE XLVI

Dissolution of Hf Metal in 0.301 N HF Acid at 30°C with NaF Addition.

	Run No. 4 0.125 M NaF T = 29.0°C P = 735.4 mm Hg			Run No. 5 0.150 M NaF T = 26.6°C P = 736.2 mm Hg			Run No. 6 0.175 M NaF T = 26.4°C P = 736.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
1	1.20	1.20	1.00	1.20	1.20	1.02	1.00	1.00	0.85
2	2.10	0.90	0.75	1.90	0.70	0.59	1.50	0.50	0.42
4	3.90	1.80	1.50	3.00	1.10	0.93	1.80	0.30	0.25
6	5.30	1.40	1.17	3.90	0.90	0.76	2.10	0.30	0.25
8	6.50	1.20	1.00	4.50	0.60	0.51	2.40	0.30	0.25
10	7.50	1.00	0.84	4.90	0.40	0.34	2.50	0.10	0.08
12	8.40	0.90	0.75	5.20	0.30	0.25	2.60	0.10	0.08
14	9.30	0.90	0.75	5.30	0.10	0.08*	2.70	0.10	0.08
16	10.00	0.70	0.58	5.40	0.10	0.08*	2.70	0.00	0.00
18	10.80	0.80	0.67	5.60	0.20	0.17*	2.80	0.10	0.08*
20	11.40	0.60	0.50	5.60	0.00	0.00*	2.80	0.00	0.00*
22	11.80	0.40	0.33*	5.70	0.10	0.08*	2.90	0.10	0.08*
24	12.20	0.40	0.33*	5.80	0.10	0.08*	2.90	0.00	0.00*
26	12.60	0.40	0.33*	5.80	0.00	0.00*	3.00	0.10	0.08*
28	13.00	0.40	0.33*						
Ave. Rate (ml/min)			0.16			0.04			0.02

* Values averaged to get average maximum rate.

TABLE XLVII

Dissolution of Hf Metal in 0.301 N HF Acid at 30°C with NaF Addition.

	Run No. 7 0.200 M NaF T = 25.0°C P = 736.6 mm Hg			Run No. 8 0.300 M NaF T = 25.4°C P = 735.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	0.80	0.80	0.68	0.70	0.70	0.60
2	0.90	0.10	0.09	0.90	0.20	0.17
4	1.00	0.10	0.09	1.00	0.10	0.09
6	1.20	0.20	0.17	1.20	0.20	0.17
8	1.30	0.10	0.09	1.30	0.10	0.09
10	1.40	0.10	0.09	1.40	0.10	0.09
12	1.50	0.10	0.09	1.40	0.00	0.00*
14	1.50	0.00	0.00	1.40	0.00	0.00*
16	1.60	0.10	0.09*	1.40	0.00	0.00*
18	1.60	0.00	0.00*	1.40	0.00	0.00*
20	1.60	0.00	0.00*	1.40	0.00	0.00*
22	1.70	0.10	0.09*	1.40	0.00	0.00*
24	1.70	0.00	0.00*	1.40	0.00	0.00*
26	1.70	0.00	0.00*	1.40	0.00	0.00*
Ave. Rate (ml/min)			0.02			0.00

* Values averaged to get average maximum rate.

TABLE XLVIII

Dissolution of Hf Metal in 0.304 N HF and 1.00 N HCl Acid Mixture at 30°C with NaF Addition.

	Run No. 1 0.050 M NaF T = 24.7°C P = 743.2 mm Hg			Run No. 2 0.100 M NaF T = 24.5°C P = 744.5 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
3	4.40	4.40	3.81	5.50	5.50	4.77*
6	9.00	4.60	3.98*	10.90	5.40	4.69*
9	13.60	4.60	3.98*	16.20	5.30	4.60*
12	18.20	4.60	3.98*	21.40	5.20	4.51*
15	22.70	4.50	3.89*	26.70	5.30	4.60*
18	27.20	4.50	3.89*	31.90	5.20	4.51*
21	31.60	4.40	3.81	37.20	5.30	4.60*
24	35.90	4.30	3.72	42.40	5.20	4.51*
27	40.10	4.20	3.63	47.50	5.10	4.42
30	44.30	4.20	3.63	52.80	5.30	4.60
33	48.60	4.30	3.72	57.90	5.10	4.42
36	52.90	4.30	3.72	63.00	5.10	4.42
39	57.40	4.50	3.89			
42	61.80	4.40	3.81			
Ave. Rate (ml/min)			1.31			1.53

* Values averaged to get average maximum rate.

TABLE XLIX

Dissolution of Hf Metal in 0.304 N HF and 1.00 N HCl Acid Mixture at 30°C with NaF Addition.

	Run No. 3 0.250 M NaF T = 25.5°C P = 738.4 mm Hg			Run No. 4 0.400 M NaF T = 24.0°C P = 734.1 mm Hg			Run No. 5 0.450 M NaF T = 25.0°C P = 741.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
1	2.00	2.00	1.71	2.60	2.60	2.23	2.90	2.90	2.50
2	4.30	2.30	1.97	5.40	2.80	2.40	5.70	2.80	2.41
3	6.70	2.40	2.05*	8.30	2.90	2.49	8.60	2.90	2.50
4	9.00	2.30	1.97*	11.10	2.80	2.40	11.60	3.00	2.58*
5	11.30	2.30	1.97*	14.00	2.90	2.49*	14.60	3.00	2.58*
6	13.70	2.40	2.05*	17.10	3.10	2.66*	17.60	3.00	2.58*
7	16.10	2.40	2.05*	20.10	3.00	2.57*	20.50	2.90	2.50
8	18.40	2.30	1.97	23.00	2.90	2.49	23.40	2.90	2.50
9	20.70	2.30	1.97	25.90	2.90	2.49	26.10	2.70	2.32
10	23.00	2.30	1.97	28.70	2.80	2.40	28.90	2.80	2.41
11	25.30	2.30	1.97	31.50	2.80	2.40	31.70	2.80	2.41
12	27.60	2.30	1.97	34.20	2.70	2.31	34.40	2.70	2.32
13	29.90	2.30	1.97	37.10	2.90	2.49	37.20	2.80	2.41
14	32.20	2.30	1.97	39.90	2.80	2.40	39.90	2.70	2.32
15	34.40	2.20	1.88	42.70	2.80	2.40	42.60	2.70	2.32
16	36.70	2.30	1.97				45.20	2.60	2.24
17	39.00	2.30	1.97						
18	41.30	2.30	1.97						
Ave. Rate (ml/min)			2.02			2.57			2.58

* Values averaged to get average maximum rate.

TABLE L

Dissolution of Hf Metal in 0.304 N HF and 1.00 N HCl Acid Mixture at 30°C with NaF Addition.

	Run No. 6 0.500 M NaF T = 24.9°C P = 744.7 mm Hg			Run No. 7 0.500 M NaF T = 25.0°C P = 736.1 mm Hg			Run No. 8 0.600 M NaF T = 24.5°C P = 733.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
1				2.70	2.70	2.31	3.10	3.10	2.65
2	5.50	5.50	4.76	5.60	2.90	2.48	6.30	3.20	2.73
3				8.50	2.90	2.48	9.80	3.50	2.99*
4	11.60	6.10	5.28*	11.50	3.00	2.57*	13.30	3.50	2.99*
5				14.50	3.00	2.57*	16.80	3.50	2.99*
6	17.30	5.60	4.85	17.50	3.00	2.57*	20.30	3.50	2.99*
7				20.60	3.10	2.65*	23.70	3.40	2.90
8	22.90	5.60	4.85	23.60	3.00	2.57*	26.90	3.20	2.73
9				26.60	3.00	2.57*	30.10	3.20	2.73
10	28.40	5.50	4.70	29.50	2.90	2.48	33.10	3.00	2.56
11							36.00	2.90	2.48
12	33.80	5.40	4.68				38.90	2.90	2.48
13							41.80	2.90	2.48
14	39.40	5.60	4.85				44.70	2.90	2.48
15							47.80	3.10	2.65
16	44.80	5.40	4.68				50.90	3.10	2.65
18	50.00	5.20	4.50						
20	55.00	5.00	4.33						
22	60.30	5.30	4.59						
24	65.30	5.20	4.50						
26	70.40	4.90	4.24						
28	75.30	4.90	4.24						
30	80.30	5.00	4.33						
Ave. Rate (ml/min)			2.64			2.58			2.99

* Values averaged to get average maximum rate.

TABLE LI

Dissolution of Hf Metal in 0.304 N HF and 1.00 N HCl Acid Mixture at 30°C with NaF Addition.

	Run No. 9 0.700 M NaF T = 23.8°C P = 738.9 mm Hg			Run No. 10 0.800 M NaF T = 24.0°C P = 732.9 mm Hg			Run No. 11 0.900 M NaF T = 25.2°C P = 737.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
1	3.70	3.70	3.20*	2.90	2.90	2.48*	0.70	0.70	0.60*
2	6.90	3.20	2.76	5.40	2.50	2.14	1.10	0.40	0.34
3	10.00	3.10	2.68	7.80	2.30	1.97	1.30	0.20	0.17
4	13.10	3.10	2.68	10.30	2.50	2.14	1.50	0.20	0.17
5	16.30	3.20	2.76	12.70	2.40	2.05	1.70	0.20	0.17
6	19.60	3.30	2.85	14.80	2.10	1.80	1.90	0.20	0.17
7	22.70	3.10	2.68	16.80	2.00	1.71			
8	25.70	3.00	2.59	18.50	1.70	1.45			
9	28.50	2.80	2.42	20.10	1.60	1.37	2.20	0.30	0.26
10	31.10	2.60	2.25	21.50	1.40	1.20			
11	33.60	2.50	2.16	22.70	1.20	1.03			
12	36.00	2.40	2.07	24.00	1.30	1.11	2.60	0.40	0.34
13	38.30	2.30	1.99	25.10	1.10	0.94			
14	40.50	2.20	1.90	26.00	0.90	0.77			
15	42.50	2.00	1.73	27.00	1.00	0.86	2.80	0.20	0.17
16	44.40	1.90	1.64	27.90	0.90	0.77			
17	46.80	2.40	2.07	28.90	1.00	0.86			
18	48.90	2.10	1.81	30.10	1.20	1.03	3.00	0.20	0.17
19	50.80	1.90	1.64	31.50	1.40	1.20			
20				32.60	1.10	0.94			
21				33.60	1.00	0.86			
22				34.70	1.10	0.94			
23				35.70	1.00	0.86			
Ave. Rate (ml/min)			3.20			2.48			0.60

* Values averaged to get average maximum rate.

TABLE LII

Dissolution of Hf Metal in 0.304 N HF and 1.00 N HCl Acid Mixture at 30°C with NaF Addition.

Run No. 12
1.00 M NaF
T = 26.0°C
P = 726.2 mm Hg

Time	Vol	dV	dV STP
min	ml	ml	ml
0	0.00	--	—
3	0.60	0.60	0.50*
6	0.80	0.20	0.17
9	1.00	0.20	0.17
12	1.20	0.20	0.17
15	1.40	0.20	0.17
18	1.60	0.20	0.17
21	2.00	0.40	0.33
24	2.30	0.30	0.25
27	2.50	0.20	0.17
30	2.70	0.20	0.17
Ave. Rate (ml/min)			0.17

* Values averaged to get average maximum rate.

TABLE LIII

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with KF Addition.

	Run No. 1 0.000 M KF T = 26.4°C P = 732.8 mm Hg			Run No. 2 0.100 M KF T = 26.4°C P = 733.0 mm Hg			Run No. 3 0.200 M KF T = 25.0°C P = 733.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	1.60	1.60	1.35	2.10	2.10	1.77	2.60	2.60	2.21
4	3.60	2.00	1.69*	4.40	2.30	1.94*	5.00	2.40	2.04
6	5.40	1.80	1.52*	6.60	2.20	1.86*	7.50	2.50	2.13*
8	7.10	1.70	1.44*	8.80	2.20	1.86*	10.00	2.50	2.13*
10	9.00	1.90	1.60*	11.10	2.30	1.94	12.50	2.50	2.13*
12	10.80	1.80	1.52*	13.30	2.20	1.86	15.00	2.50	2.13*
14	12.60	1.80	1.52	15.50	2.20	1.86	17.50	2.50	2.13
16	14.30	1.70	1.44	17.70	2.20	1.86	20.00	2.50	2.13
18	16.10	1.80	1.52	19.80	2.10	1.77	22.50	2.50	2.13
20	17.80	1.70	1.44	22.00	2.20	1.86	24.90	2.40	2.04
22	19.60	1.80	1.52	24.10	2.10	1.77	27.40	2.50	2.13
24	21.30	1.70	1.44	26.30	2.20	1.86	29.80	2.40	2.04
26	23.00	1.70	1.44	28.40	2.10	1.77	32.30	2.50	2.13
Ave. Rate (ml/min)			0.78			0.94			1.06

* Values averaged to get average maximum rate.

TABLE LIV

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with KF Addition.

	Run No. 4 0.300 M KF T = 28.6°C P = 738.0 mm Hg			Run No. 5 0.400 M KF T = 27.0°C P = 735.8 mm Hg			Run No. 6 0.500 M KF T = 31.2°C P = 730.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	2.40	2.40	2.02	2.20	2.20	1.86	2.20	2.20	1.80
4	5.00	2.60	2.18*	4.90	2.70	2.28*	4.70	2.50	2.04*
6	7.60	2.60	2.18*	7.50	2.60	2.20*	7.10	2.40	1.96*
8	10.20	2.60	2.18*	10.00	2.50	2.11*	9.60	2.50	2.04*
10	12.80	2.60	2.18*	12.40	2.40	2.03*	12.10	2.50	2.04*
12	15.30	2.50	2.10	15.00	2.60	2.20	14.60	2.50	2.04*
14	17.80	2.50	2.10	17.60	2.60	2.20	17.00	2.40	1.96
16	20.40	2.60	2.18	20.00	2.40	2.03	19.50	2.50	2.04
18	23.00	2.60	2.18	22.50	2.50	2.11	22.00	2.50	2.04
20	25.60	2.60	2.18	24.90	2.40	2.03	24.50	2.50	2.04
22	28.20	2.60	2.18	27.20	2.30	1.94	27.00	2.50	2.04
24	30.70	2.50	2.10	29.60	2.40	2.03	29.50	2.50	2.04
26	33.20	2.50	2.10	32.10	2.50	2.11	31.90	2.40	1.94
Ave. Rate (ml/min)			1.09			1.08			1.01

* Values averaged to get average maximum rate.

TABLE LV

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with KF Addition.

	Run No. 7 0.550 M KF T = 29.0°C P = 732.2 mm Hg			Run No. 8 0.600 M KF T = 28.2°C P = 736.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	2.20	2.20	1.83	2.20	2.20	1.85
4	4.50	2.30	1.91*	4.10	1.90	1.60
6	7.00	2.50	2.08*	5.60	1.50	1.26
8	9.40	2.40	1.99*	6.50	0.90	0.76*
10	11.80	2.40	1.99*	7.00	0.50	0.42*
12	14.20	2.40	1.99*	7.50	0.50	0.42*
14	16.50	2.30	1.91	8.10	0.60	0.50*
16	18.70	2.20	1.83	8.80	0.70	0.59*
18	20.70	2.00	1.66	9.60	0.80	0.67*
20	22.50	1.80	1.50	10.40	0.80	0.67*
22	23.90	1.40	1.16	11.20	0.80	0.67*
24	25.10	1.20	1.00	11.80	0.60	0.50*
26	26.10	1.00	0.83	12.60	0.80	0.67*
Ave. Rate (ml/min)			1.00			0.59

* Values averaged to get average maximum rate.

TABLE LVI

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with KF Addition.

	Run No. 9 0.700 M KF T = 32.0°C P = 730.4 mm Hg			Run No. 10 1.00 M KF T = 31.8°C P = 730.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	0.30	0.30	0.24	0.30	0.30	0.24
4	0.50	0.20	0.16	0.40	0.10	0.08*
6	0.60	0.10	0.08	0.50	0.10	0.08*
8	1.20	0.60	0.49*	0.60	0.10	0.08*
10	1.60	0.40	0.33*	0.80	0.20	0.16*
12	2.20	0.60	0.49*	0.90	0.10	0.08*
14	2.60	0.40	0.33*	1.10	0.20	0.16*
16	3.10	0.50	0.41	1.20	0.10	0.08*
18	3.50	0.40	0.33	1.40	0.20	0.16*
20	4.00	0.50	0.41	1.60	0.20	0.16*
22	4.40	0.40	0.33	1.80	0.20	0.16*
24	4.80	0.40	0.33	2.00	0.20	0.16*
26	5.20	0.40	0.33	2.20	0.20	0.16*
Ave. Rate (ml/min)			0.20			0.13

* Values averaged to get average maximum rate.

TABLE LVII

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 1 0.000 M NH_4F T = 27.4°C P = 735.2 mm Hg			Run No. 2 0.100 M NH_4F T = 28.8°C P = 729.6 mm Hg			Run No. 3 0.200 M NH_4F T = 27.8°C P = 726.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	1.50	1.50	1.26	1.80	1.80	1.49	2.00	2.00	1.66
4	3.30	1.80	1.52*	3.90	2.10	1.74*	4.30	2.30	1.91*
6	4.90	1.60	1.35*	6.00	2.10	1.74*	6.70	2.40	1.99*
8	6.70	1.80	1.52*	8.10	2.10	1.74*	9.10	2.40	1.99*
10	8.40	1.70	1.43*	10.20	2.10	1.74*	11.40	2.30	1.91*
12	10.20	1.80	1.52*	12.30	2.10	1.74*	13.80	2.40	1.99*
14	11.90	1.70	1.43*	14.40	2.10	1.74*	16.10	2.30	1.91
16	13.60	1.70	1.43	16.50	2.10	1.74*	19.40	2.30	1.91
18	15.40	1.80	1.52	18.60	2.10	1.74*	20.70	2.30	1.91
20	17.10	1.70	1.43	20.60	2.00	1.66	23.00	2.30	1.91
22	18.90	1.80	1.52	22.60	2.00	1.66	25.20	2.20	1.83
24	20.40	1.50	1.26	24.60	2.00	1.66	27.50	2.30	1.91
26	22.10	1.70	1.43	26.60	2.00	1.66	29.70	2.20	1.83
Ave. Rate (ml/min)			0.73			0.77			0.98

* Values averaged to get average maximum rate.

TABLE LVIII

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 4 0.300 M NH_4F T = 28.0°C P = 727.0 mm Hg			Run No. 5 0.400 M NH_4F T = 27.6°C P = 728.4 mm Hg			Run No. 6 0.500 M NH_4F T = 27.0°C P = 735.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	2.20	2.20	1.83	2.00	2.00	1.67	2.60	2.60	2.20
4	5.00	2.80	2.32*	4.30	2.30	1.92*	4.90	2.30	1.94
6	7.60	2.60	2.16*	6.50	2.20	1.83*	7.40	2.50	2.11*
8	10.20	2.60	2.16*	8.60	2.10	1.75*	9.90	2.50	2.11*
10	12.80	2.60	2.16*	10.70	2.10	1.75*	12.40	2.50	2.11*
12	15.20	2.40	1.99	12.80	2.10	1.75*	14.80	2.40	2.03*
14	17.80	2.60	2.16	15.00	2.20	1.83*	17.30	2.50	2.11*
16	20.30	2.50	2.08	17.00	2.00	1.67	19.80	2.50	2.11*
18	22.80	2.50	2.08	19.10	2.10	1.75	22.20	2.40	2.03*
20	25.10	2.30	1.91	21.20	2.10	1.75	24.60	2.40	2.03
22	27.40	2.30	1.91	23.30	2.10	1.75	27.20	2.60	2.20
24	29.90	2.50	2.08	25.40	2.10	1.75	29.60	2.40	2.03
26	32.20	2.30	1.91	27.40	2.10	1.75	32.00	2.40	2.03
Ave. Rate (ml/min)			1.10			0.90			1.04

* Values averaged to get average maximum rate.

TABLE LIX

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 7 0.700 M NH_4F T = 27.0°C P = 735.4 mm Hg			Run No. 8 1.00 M NH_4F T = 27.4°C P = 737.2 mm Hg			Run No. 9 1.50 M NH_4F T = 28.0°C P = 737.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	2.40	2.40	2.03	2.70	2.70	2.28	2.60	2.60	2.19
4	5.00	2.60	2.20*	5.40	2.70	2.28*	5.20	2.60	2.19
6	7.50	2.50	2.11*	8.00	2.60	2.20*	7.90	2.70	2.27
8	9.90	2.40	2.03*	10.50	2.50	2.11*	10.70	2.80	2.36*
10	12.40	2.50	2.11*	13.10	2.60	2.20*	13.50	2.80	2.36*
12	14.90	2.50	2.11*	15.80	2.70	2.28*	16.30	2.80	2.36*
14	17.40	2.50	2.11*	18.40	2.60	2.20*	19.10	2.80	2.36*
16	19.80	2.40	2.03*	20.90	2.50	2.11	21.90	2.80	2.36*
18	22.30	2.50	2.11	23.60	2.70	2.28	24.70	2.80	2.36*
20	24.70	2.40	2.03	26.20	2.60	2.20	27.50	2.80	2.36*
22	27.20	2.50	2.11	28.90	2.70	2.28	30.20	2.70	2.27
24	29.40	2.20	1.86	31.50	2.60	2.20	33.00	2.80	2.36
26	31.90	2.50	2.11	34.10	2.60	2.20	35.70	2.70	2.27
28	34.40	2.50	2.11						
30	36.70	2.30	1.94						
Ave. Rate (ml/min)			1.05			1.11			1.18

* Values averaged to get average maximum rate.

TABLE LX

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 10 2.00 M NH_4F T = 28.0°C P = 733.6 mm Hg			Run No. 11 3.00 M NH_4F T = 29.0°C P = 733.8 mm Hg			Run No. 12 3.50 M NH_4F T = 32.0°C P = 731.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	2.80	2.80	2.35	2.70	2.70	2.25	2.00	2.00	1.63
4	5.50	2.70	2.26*	5.40	2.70	2.25	3.90	1.90	1.55*
6	8.20	2.70	2.26*	8.20	2.80	2.33	5.60	1.70	1.39*
8	11.00	2.80	2.35*	10.90	2.70	2.25	7.50	1.90	1.55*
10	13.70	2.70	2.26*	13.70	2.80	2.33*	9.20	1.70	1.39*
12	16.40	2.70	2.26*	16.60	2.90	2.42*	11.20	2.00	1.63*
14	19.10	2.70	2.26*	19.40	2.80	2.33*	13.00	1.80	1.47
16	21.80	2.70	2.26*	22.30	2.90	2.42*	15.10	2.10	1.71
18	24.60	2.80	2.35*	25.10	2.80	2.33*	17.10	2.00	1.63
20	27.30	2.70	2.26	28.00	2.90	2.42*	19.00	1.90	1.55
22	30.10	2.80	2.35	30.90	2.90	2.42	21.10	2.10	1.71
24	32.80	2.70	2.26	33.70	2.80	2.33	23.00	1.90	1.55
26	35.50	2.70	2.26	36.50	2.80	2.33	25.10	2.10	1.71
Ave. Rate (ml/min)			1.14			1.19			0.75

* Values averaged to get average maximum rate.

TABLE LXI

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 13 4.00 M NH_4F T = 30.0°C P = 733.6 mm Hg			Run No. 14 5.00 M NH_4F T = 30.0°C P = 733.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
1	0.90	0.90	0.75			
2	1.60	0.70	0.58	0.80	0.80	0.66
4	2.80	1.20	0.99*	1.60	0.80	0.66*
6	3.90	1.10	0.91*	2.30	0.70	0.58*
8	5.20	1.30	1.08*	2.90	0.60	0.50*
10	6.30	1.10	0.91*	3.60	0.70	0.58*
12	7.60	1.30	1.08*	4.30	0.70	0.58*
14	9.00	1.40	1.16*	5.00	0.70	0.58*
16	10.20	1.20	0.99	5.70	0.70	0.58
18	11.40	1.20	0.99	6.50	0.80	0.66
20	12.60	1.20	0.99	7.30	0.80	0.66
22	14.00	1.40	1.16	8.10	0.80	0.66
24	15.10	1.10	0.91	8.90	0.80	0.66
26	16.40	1.30	1.08	9.60	0.70	0.58
Ave. Rate (ml/min)			0.51			0.29

* Values averaged to get average maximum rate.

TABLE LXII

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C with NH_4F Addition.

	Run No. 15 6.00 M NH_4F T = 31.0°C P = 733.0 mm Hg			Run No. 16 8.00 M NH_4F T = 32.0°C P = 732.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
2	0.60	0.60	0.49	0.50	0.50	0.41
4	1.10	0.50	0.41*	0.90	0.40	0.33*
6	1.50	0.40	0.33*	1.10	0.20	0.16*
8	1.90	0.40	0.33*	1.20	0.10	0.08*
10	2.30	0.40	0.33*	1.50	0.30	0.24*
12	2.60	0.30	0.25*	1.60	0.10	0.08*
14	3.10	0.50	0.41*	1.80	0.20	0.16
16	3.50	0.40	0.33*	2.00	0.20	0.16
18	4.00	0.50	0.41	2.20	0.20	0.16
20	4.40	0.40	0.33	2.40	0.20	0.16
22	4.90	0.50	0.41	2.80	0.40	0.33
24	5.30	0.40	0.33	3.00	0.20	0.16
26	5.80	0.50	0.41	3.20	0.20	0.16
Ave. Rate (ml/min)			0.17			0.09

* Values averaged to get average maximum rate.

TABLE LXIII

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with Li_2SO_4 Addition.

	Run No. 1 0.000 N Li_2SO_4 T = 28.0°C P = 730.4 mm Hg			Run No. 2 0.100 N Li_2SO_4 T = 27.6°C P = 737.0 mm Hg			Run No. 3 0.200 N Li_2SO_4 T = 29.0°C P = 735.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	—	—	0.00	—	—
2	1.70	1.70	1.42	1.50	1.50	1.27	1.40	1.40	1.17
4	3.40	1.70	1.42	3.00	1.50	1.27	2.90	1.50	1.25
6	5.20	1.80	1.50*	4.60	1.60	1.35*	4.50	1.60	1.34*
8	7.00	1.80	1.50*	6.20	1.60	1.35*	6.00	1.50	1.25*
10	8.90	1.90	1.58*	7.80	1.60	1.35*	7.60	1.60	1.34*
12	10.80	1.90	1.58*	9.30	1.50	1.27*	9.20	1.60	1.34*
14	12.60	1.80	1.50	11.00	1.70	1.43*	10.70	1.50	1.25*
16	14.50	1.90	1.58	12.60	1.60	1.35*	12.30	1.60	1.34
18	16.00	1.50	1.25	14.10	1.50	1.27	13.90	1.60	1.34
20	17.70	1.70	1.42	15.60	1.50	1.27	15.40	1.50	1.25
22	19.40	1.70	1.42	17.20	1.60	1.35	17.00	1.60	1.34
24	21.10	1.70	1.42	18.90	1.70	1.43	18.60	1.60	1.34
26	22.80	1.70	1.42	20.60	1.70	1.43	20.10	1.50	1.25
28				22.20	1.60	1.35			
30				23.80	1.60	1.35			
Ave. Rate (ml/min)			0.77			0.68			0.65

* Values averaged to get average maximum rate.

TABLE LXIV

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with Li_2SO_4 Addition.

	Run No. 4 0.300 N Li_2SO_4 T = 30.0°C P = 737.4 mm Hg			Run No. 5 0.400 N Li_2SO_4 T = 30.6°C P = 737.0 mm Hg			Run No. 6 0.500 N Li_2SO_4 T = 32.2°C P = 736.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
2	1.60	1.60	1.33*	1.40	1.40	1.16	1.20	1.20	0.98
4	3.10	1.50	1.25*	2.90	1.50	1.24*	2.70	1.50	1.23
6	4.70	1.60	1.33*	4.40	1.50	1.24*	4.20	1.50	1.23*
8	6.20	1.50	1.25*	5.90	1.50	1.24*	5.80	1.60	1.31*
10	7.80	1.60	1.33*	7.40	1.50	1.24*	7.30	1.50	1.23*
12	9.30	1.50	1.25	9.00	1.60	1.33*	8.80	1.50	1.23*
14	10.80	1.50	1.25	10.40	1.40	1.16	10.40	1.60	1.31*
16	12.30	1.50	1.25	11.90	1.50	1.24	11.90	1.50	1.23
18	13.80	1.50	1.25	13.40	1.50	1.24	13.40	1.50	1.23
20	15.40	1.60	1.33	14.80	1.40	1.16	15.00	1.60	1.31
22	16.90	1.50	1.25	16.30	1.50	1.24	16.50	1.50	1.23
24	18.40	1.50	1.25	17.80	1.50	1.24	17.90	1.40	1.15
26	20.00	1.60	1.33	19.30	1.50	1.24	19.40	1.50	1.23
Ave. Rate (ml/min)			0.65			0.63			0.63

* Values averaged to get average maximum rate.

TABLE LXV

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with Li_2SO_4 Addition.

	Run No. 7 0.700 N Li_2SO_4 T = 28.4°C P = 736.4 mm Hg			Run No. 8 0.900 N Li_2SO_4 T = 28.4°C P = 735.2 mm Hg			Run No. 9 1.100 N Li_2SO_4 T = 28.4°C P = 732.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	1.30	1.30	1.09	1.20	1.20	1.01	1.10	1.10	0.92
4	2.60	1.30	1.09	2.40	1.20	1.01	2.30	1.20	1.00*
6	4.00	1.40	1.17*	3.60	1.20	1.01*	3.50	1.20	1.00*
8	5.40	1.40	1.17*	4.90	1.30	1.09*	4.70	1.20	1.00*
10	6.80	1.40	1.17*	6.20	1.30	1.09*	5.90	1.20	1.00*
12	8.20	1.40	1.17*	7.40	1.20	1.01*	7.10	1.20	1.00*
14	9.60	1.40	1.17*	8.70	1.30	1.09*	8.20	1.10	0.92
16	11.10	1.50	1.26*	9.90	1.20	1.01	9.40	1.20	1.00
18	12.50	1.40	1.17*	11.10	1.20	1.01	10.60	1.20	1.00
20	13.80	1.30	1.09	12.40	1.30	1.09	11.70	1.10	0.92
22	15.00	1.20	1.01	13.70	1.30	1.09	12.90	1.20	1.00
24	16.30	1.30	1.09	15.00	1.30	1.09	14.00	1.10	0.92
26	17.60	1.30	1.09	16.20	1.20	1.01	15.10	1.10	0.92
Ave. Rate (ml/min)			0.59			0.53			0.50

* Values averaged to get average maximum rate.

TABLE LXVI

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with Li_2SO_4 Addition.

	Run No. 10 1.300 N Li_2SO_4 T = 27.6°C P = 731.2 mm Hg			Run No. 11 1.500 N Li_2SO_4 T = 26.7°C P = 732.0 mm Hg			Run No. 12 1.700 N Li_2SO_4 T = 27.0°C P = 731.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
2	0.80	0.80	0.67	1.00	1.00	0.84	1.00	1.00	0.84
4	1.80	1.00	0.84*	2.10	1.10	0.93*	1.90	0.90	0.76*
6	2.80	1.00	0.84*	3.20	1.10	0.93*	2.80	0.90	0.76*
8	3.80	1.00	0.84*	4.20	1.00	0.84*	3.80	1.00	0.84*
10	4.70	0.90	0.75*	5.20	1.00	0.84*	4.70	0.90	0.76
12	5.70	1.00	0.84*	6.10	0.90	0.76	5.60	0.90	0.76
14	6.70	1.00	0.84*	7.00	0.90	0.76	6.50	0.90	0.76
16	7.60	0.90	0.75*	8.00	1.00	0.84	7.40	0.90	0.76
18	8.60	1.00	0.84	9.00	1.00	0.84	8.20	0.80	0.67
20	9.60	1.00	0.84	10.00	1.00	0.84	9.20	1.00	0.84
22	10.60	1.00	0.84	11.00	1.00	0.84	10.00	0.80	0.67
24	11.60	1.00	0.84	11.90	0.90	0.76	11.00	1.00	0.84
26	12.50	0.90	0.75	12.80	0.90	0.76	11.90	0.90	0.76
Ave. Rate (ml/min)			0.41			0.44			0.39

* Values averaged to get average maximum rate.

TABLE LXVII

Dissolution of Hf Metal in 0.299 N HF Acid at 30°C with Li_2SO_4 Addition.

Run No. 13
1.900 N Li_2SO_4
T = 27.8°C
P = 731.4 mm Hg

Time	Vol	dV	dV STP
min	ml	ml	ml
0	0.00	--	--
2	1.00	1.00	0.84
4	2.10	1.10	0.92*
6	3.20	1.10	0.92*
8	4.40	1.20	1.00*
10	5.60	1.20	1.00*
12	6.70	1.10	0.92*
14	7.80	1.10	0.92*
16	8.90	1.10	0.92
18	10.00	1.10	0.92
20	11.10	1.10	0.92
22	12.20	1.10	0.92
24	13.40	1.20	1.00
26	14.50	1.10	0.92
Ave. Rate (ml/min)			0.47

* Values averaged to get average maximum rate.

TABLE LXVIII

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C

with Noble Metal Addition.

Run No. 1
0.005 N Pt^{+4}
T = 27.4°C
P = 735.0 mm Hg

Time	Vol	dV	dV STP	Time	Vol	dV	dV STP
min	ml	ml	ml	min	ml	ml	ml
0	0.00	--	--	50	7.50	-0.10	-0.08
2	1.70	1.70	1.43	52	7.40	-0.10	-0.08
4	3.30	1.60	1.35	54	7.20	-0.20	-0.17
6	5.20	1.90	1.60	56	7.20	0.00	0.00
8	6.90	1.70	1.43	58	7.20	0.00	0.00
10	8.70	1.80	1.52	60	7.20	0.00	0.00
12[a]	10.50	1.80	1.52	62	7.30	0.10	0.08
14	9.80	-0.70	-0.59	64	7.70	0.40	0.34
16	9.80	0.00	0.00	66	8.30	0.70	0.59
18	9.70	-0.10	-0.08	68	9.00	0.70	0.59
20	9.70	0.00	0.00	70	9.90	0.90	0.76
22	9.60	-0.10	-0.08	72	10.90	1.00	0.84
24	9.50	-0.10	-0.08	74	11.80	0.90	0.76
26	9.40	-0.10	-0.08	76	12.80	1.00	0.84
28	9.20	-0.20	-0.17	78	13.80	1.00	0.84
30	9.10	-0.10	-0.08	80	14.80	1.00	0.84
32	8.90	-0.20	-0.17	82	15.80	1.00	0.84
34	8.80	-0.10	-0.08	84	16.90	1.10	0.93
36	8.60	-0.20	-0.17	86	17.90	1.00	0.84
38	8.40	-0.20	-0.17	88	19.00	1.10	0.93
40	8.20	-0.20	-0.17	90	19.90	0.90	0.76
42	8.10	-0.10	-0.08	92	21.00	1.10	0.93
44	8.00	-0.10	-0.08	94	22.00	1.00	0.84
46	7.80	-0.20	-0.17	96	23.00	1.00	0.84
48	7.60	-0.20	-0.17	98	24.00	1.00	0.84
				100	25.00	1.00	0.84

[a] Added 1.942 gm of 10% $H_2PtCl_6 \cdot 6H_2O$ solution.

TABLE LXIX

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C

with Noble Metal Addition.

Run No. 2
0.005 N Au^{+3}
T = 28.4°C
P = 741.0 mm Hg

Time	Vol	dV	dV STP	Time	Vol	dV	dV STP
min	ml	ml	ml	min	ml	ml	ml
0	0.00	—	—	50	37.40	1.40	1.18
2	1.80	1.80	1.52	52	38.60	1.20	1.01
4	3.60	1.80	1.52	54	39.90	1.30	1.10
6	5.30	1.70	1.44	56	41.20	1.30	1.10
8	7.10	1.80	1.52	58	42.40	1.20	1.01
10	8.90	1.80	1.52	60	43.70	1.30	1.10
12[a]	10.70	1.80	1.52	62	45.00	1.30	1.10
14	12.20	1.50	1.27	64	46.20	1.20	1.01
16	13.60	1.40	1.18	66	47.50	1.30	1.10
18	15.00	1.40	1.18	68	48.70	1.20	1.01
20	16.40	1.40	1.18	70	50.00	1.30	1.10
22	17.90	1.50	1.27	72	51.20	1.20	1.01
24	19.40	1.50	1.27	74	52.40	1.20	1.01
26	20.80	1.40	1.18	76	53.70	1.30	1.10
28	22.20	1.40	1.18	78	54.90	1.20	1.01
30	23.60	1.40	1.18	80	56.20	1.30	1.10
32	25.00	1.40	1.18	82	57.40	1.20	1.01
34	26.50	1.50	1.27	84	58.60	1.20	1.01
36	28.00	1.50	1.27	86	59.80	1.20	1.01
38	29.30	1.30	1.10	88	61.00	1.20	1.01
40	30.70	1.40	1.18	90	62.20	1.20	1.01
42	32.00	1.30	1.10	92	63.40	1.20	1.01
44	33.30	1.30	1.10	94	64.60	1.20	1.01
46	34.60	1.30	1.10	96	65.80	1.20	1.01
48	36.00	1.40	1.18	98	66.90	1.10	0.93
				100	68.10	1.20	1.01

[a] Added 49.8 ml of 3.5 gm/l $AuCl_3$ solution.

TABLE LXX

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C

with Noble Metal Addition.

Run No. 3
0.005 N Ag^{+1}
T = 29.4°C
P = 740.6 mm Hg

Time	Vol	dV	dV STP	Time	Vol	dV	dV STP
min	ml	ml	ml	min	ml	ml	ml
0	0.00	—	—	50	31.80	1.00	0.84
2	1.80	1.80	1.51	52	32.80	1.00	0.84
4	3.60	1.80	1.51	54	33.80	1.00	0.84
6	5.50	1.90	1.59	56	34.80	1.00	0.84
8	7.40	1.90	1.59	58	35.80	1.00	0.84
10	9.20	1.80	1.51	60	36.80	1.00	0.84
12[a]	11.10	1.90	1.59	62	37.80	1.00	0.84
14	12.50	1.40	1.17	64	38.80	1.00	0.84
16	13.60	1.10	0.92	66	39.80	1.00	0.84
18	14.80	1.20	1.01	68	40.90	1.10	0.92
20	15.90	1.10	0.92	70	41.90	1.00	0.84
22	17.00	1.10	0.92	72	42.90	1.00	0.84
24	18.10	1.10	0.92	74	43.80	0.90	0.76
26	19.20	1.10	0.92	76	44.70	0.90	0.76
28	20.30	1.10	0.92	78	45.60	0.90	0.76
30	21.40	1.10	0.92	80	46.60	1.00	0.84
32	22.40	1.00	0.84	82	47.20	0.60	0.50
34	23.40	1.00	0.84	84	48.20	1.00	0.84
36	24.40	1.00	0.84	86	49.20	1.00	0.84
38	25.50	1.10	0.92	88	50.30	1.10	0.92
40	26.60	1.10	0.92	90	51.40	1.10	0.92
42	27.70	1.10	0.92	92	52.40	1.00	0.84
44	28.80	1.10	0.92	94	53.40	1.00	0.84
46	29.80	1.00	0.84	96	54.50	1.10	0.92
48	30.80	1.00	0.84	98	55.50	1.00	0.84
				100	56.50	1.00	0.84

[a] Added 3.0 ml of 0.50 N $AgNO_3$ solution.

TABLE LXXI

Dissolution of Hf Metal in 0.300 N HF and 1.00 N HCl Acid Mixture at 30°C with $PtCl_4$ Addition.

T = 24.0°C
P = 739.8 mm Hg

Time	Vol	dV	dV STP	Time	Vol	dV	dV STP
min	ml	ml	ml	min	ml	ml	ml
0	0.00	--	--	32	35.70	2.20	1.90
2	1.80	1.80	1.56	34	37.90	2.20	1.90
4	4.10	2.30	1.99	36	40.20	2.20	1.99
6	6.40	2.30	1.99	38	42.40	2.20	1.90
8	8.60	2.20	1.90	40	44.60	2.20	1.90
10	10.90	2.30	1.99	42	46.80	2.20	1.90
12*	13.20	2.30	1.99	44	49.10	2.30	1.99
13	13.90	0.70	0.61	46	51.40	2.30	1.99
14	15.00	1.10	0.95	48	53.60	2.20	1.90
16	17.30	2.30	1.99	50	55.90	2.30	1.99
18	19.70	2.40	2.07	52	58.30	2.40	2.07
20	21.90	2.20	1.90	54	60.60	2.30	1.99
22	24.20	2.30	1.99	56	62.90	2.30	1.99
24	26.50	2.30	1.99	58	65.20	2.30	1.99
26	29.00	2.50	2.16	60	67.50	2.30	1.99
28	31.40	2.40	2.07				
30	33.50	2.10	1.82				

* Added 0.75 ml of 0.500 M $PtCl_4$ solution.

TABLE LXXII

Dissolution of Hf Metal in 0.301 N HF at 30°C with Oxidising Agent Additions.

	Run No. 1 0.0529 N $NaBiO_3$ T = 29.9°C P = 731.3 mm Hg			Run No. 2 0.0529 N $KMnO_4$ T = 31.4°C P = 731.8 mm Hg			Run No. 3 0.0529 N $K_2Cr_2O_7$ T = 32.6°C P = 731.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	1.50	1.50	1.24	1.60	1.60	1.31	1.40	1.40	1.14
4	3.30	1.80	1.49	3.30	1.70	1.39	3.20	1.80	1.46
6	5.20	1.90	1.57	5.20	1.90	1.56	5.10	1.90	1.54
8	7.20	2.00	1.65	7.20	2.00	1.64	7.00	1.90	1.54
10	9.20	2.00	1.65	9.10	1.90	1.56	8.80	1.80	1.46
12[a]	11.20	2.00	1.65	11.00	1.90	1.56	10.70	1.90	1.54
14	13.50	2.30	1.90	12.80	1.80	1.47	11.40	0.70	0.57
16	15.40	1.90	1.57	13.90	1.10	0.90	11.90	0.50	0.41
18	17.00	1.60	1.32	14.80	0.90	0.74	12.30	0.40	0.32
20	18.60	1.60	1.32	15.70	0.90	0.74	13.00	0.70	0.57
22	20.10	1.50	1.24	16.70	1.00	0.82	13.50	0.50	0.41
24	21.40	1.30	1.07	17.60	0.90	0.74	14.00	0.50	0.41
26	22.60	1.20	0.99	18.40	0.80	0.65	14.80	0.80	0.65
28	23.90	1.30	1.07	19.30	0.90	0.74			
30	25.10	1.20	0.99						
32	26.20	1.10	0.91						
34	27.20	1.00	0.83						

[a] Added 2.220 gm of $NaBiO_3$ to the reaction mixture in Run No. 1.
[a] Added 0.501 gm of $KMnO_4$ to the reaction mixture in Run No. 2.
[a] Added 1.556 gm of $K_2Cr_2O_7$ to the reaction mixture in Run No. 3.

TABLE LXXIII

Dissolution of Hf Metal in 0.300 N HF Acid at 30°C

with Mineral Acid Addition.

	Run No. 1 0.100 N HCl T = 34.2°C P = 733.0 mm Hg			Run No. 2 0.100 N H_2SO_4 T = 33.0°C P = 733.6 mm Hg			Run No. 3 0.100 N H_3PO_4 T = 28.0°C P = 738.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
2	1.30	1.30	1.05	1.60	1.60	1.30	1.60	1.60	1.35
4	3.00	1.70	1.37	3.40	1.80	1.46	3.40	1.80	1.52
6	4.90	1.90	1.53	5.30	1.90	1.54	5.30	1.90	1.60
8	6.70	1.80	1.45	7.20	1.90	1.54	7.20	1.90	1.60
10	8.60	1.90	1.53	9.10	1.90	1.54	9.10	1.90	1.60
12*	10.50	1.90	1.53	11.00	1.90	1.54	11.10	2.00	1.69
14	12.60	2.10	1.69	13.00	2.00	1.63	13.00	1.90	1.60
16	14.70	2.10	1.69	14.80	1.80	1.46	14.80	1.80	1.52
18	16.80	2.10	1.69	16.60	1.80	1.46	16.60	1.80	1.52
20	18.70	1.90	1.53	18.50	1.90	1.54	18.40	1.80	1.52
22	20.80	2.10	1.69	20.40	1.90	1.54	20.10	1.70	1.43
24	22.80	2.00	1.61	22.20	1.80	1.46	22.00	1.90	1.60
26	24.80	2.00	1.61	24.00	1.80	1.46	23.60	1.60	1.35
28	26.80	2.00	1.61	25.90	1.90	1.54	25.30	1.70	1.43
30	28.80	2.00	1.61	27.80	1.90	1.54	27.20	1.90	1.60
32	30.80	2.00	1.61	29.60	1.80	1.46	28.90	1.70	1.43
34	32.70	1.90	1.53	31.50	1.90	1.54	30.60	1.70	1.43
36	34.70	2.00	1.61	33.40	1.90	1.54	32.30	1.70	1.43
38	36.70	2.00	1.61	35.20	1.80	1.46	34.00	1.70	1.43
40	38.70	2.00	1.61	37.10	1.90	1.54	35.80	1.80	1.52
42	40.70	2.00	1.61	39.00	1.90	1.54	37.50	1.70	1.43
44	42.70	2.00	1.61	40.80	1.80	1.46	39.20	1.70	1.43
46	44.60	1.90	1.53	42.70	1.90	1.54	40.90	1.70	1.43

* Added 2.65 ml of conc. hydrochloric acid to Run No. 1.
Added 0.85 ml of conc. sulfuric acid to Run No. 2.
Added 0.68 ml of conc. phosphoric acid to Run No. 3.

TABLE LXXIV

Dissolution of Hf Metal in 0.300 N HF and HCl Acid Mixture at 25°C.

	Run No. 1 0.00 N HCl T = 23.2°C P = 729.6 mm Hg			Run No. 2 0.25 N HCl T = 23.0°C P = 730.2 mm Hg			Run No. 3 0.50 N HCl T = 25.0°C P = 734.6 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
3	2.20	2.20	1.88	2.20	2.20	1.89	2.30	2.30	1.96
6	4.50	2.30	1.97*	5.00	2.80	2.40*	5.30	3.00	2.56*
9	6.80	2.30	1.97*	7.70	2.70	2.31*	8.20	2.90	2.47*
12	9.10	2.30	1.97*	10.30	2.60	2.23*	11.10	2.90	2.47*
15	11.50	2.40	2.05*	13.00	2.70	2.31*	14.00	2.90	2.47*
18	13.80	2.30	1.97*	15.80	2.80	2.40*	17.00	3.00	2.56*
21	16.20	2.40	2.05*	18.50	2.70	2.31*	19.80	2.80	2.39*
24	18.50	2.30	1.97*	21.20	2.70	2.31*	22.60	2.80	2.39*
27	20.80	2.30	1.97*	23.80	2.60	2.23*	25.50	2.90	2.47*
30	23.10	2.30	1.97*	26.50	2.70	2.31*	28.30	2.80	2.39*
Ave. Rate (ml/min)			0.663			0.771			0.821

* Values averaged to get average maximum rate.

TABLE LXXV

Dissolution of Hf Metal in 0.300 N HF and HCl Acid Mixture at 25°C.

	Run No. 4 1.00 N HCl T = 25.8°C P = 735.0 mm Hg			Run No. 5 1.50 N HCl T = 23.8°C P = 739.2 mm Hg			Run No. 6 2.00 N HCl T = 23.8°C P = 740.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—	0.00	—	—
3	2.50	2.50	2.13	2.50	2.50	2.16	2.70	2.70	2.34
6	5.60	3.10	2.64*	5.70	3.20	2.76*	5.90	3.20	2.77*
9	8.60	3.00	2.55*	8.80	3.10	2.68*	9.20	3.30	2.86*
12	11.70	3.10	2.64*	12.00	3.20	2.76*	12.50	3.30	2.86*
15	14.80	3.10	2.64*	15.10	3.10	2.68*	15.70	3.20	2.77*
18	18.00	3.20	2.72*	18.20	3.10	2.68*	18.90	3.20	2.77*
21	21.10	3.10	2.64*	21.30	3.10	2.68*	22.20	3.30	2.86*
24	24.10	3.00	2.55*	24.30	3.00	2.59*	25.50	3.30	2.86*
27	27.10	3.00	2.55*	27.40	3.10	2.68*	28.80	3.30	2.86*
30	30.20	3.10	2.64*	30.60	3.20	2.76*	32.00	3.20	2.77*
Ave. Rate (ml/min)			0.873			0.899			0.940

* Values averaged to get average maximum rate.

TABLE LXXVI

Dissolution of Hf Metal in 0.300 N HF and HCl Acid Mixture at 25°C.

	Run No. 7 2.50 N HCl T = 24.0°C P = 742.6 mm Hg			Run No. 8 4.00 N HCl T = 24.0°C P = 743.8 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
3	2.70	2.70	2.34	2.90	2.90	2.52
6	6.00	3.30	2.86*	6.20	3.30	2.87
9	9.30	3.30	2.86*	9.70	3.50	3.04*
12	12.60	3.30	2.86*	13.20	3.50	3.04*
15	15.90	3.30	2.86*	16.70	3.50	3.04*
18	19.30	3.40	2.95*	20.20	3.50	3.04*
21	22.70	3.40	2.95*	23.60	3.40	2.95*
24	26.10	3.40	2.95*	27.20	3.60	3.13*
27	29.30	3.20	2.78*	30.60	3.40	2.95*
30	32.60	3.30	2.86*	34.00	3.40	2.95*
Ave. Rate (ml/min)			0.960			1.006

* Values averaged to get average maximum rate.

TABLE LXXVII

Dissolution of Hf Metal in 0.300 N HF and HCl Acid Mixture at 25°C.

	Run No. 9 6.00 N HCl T = 24.0°C P = 742.0 mm Hg			Run No. 10 8.00 N HCl T = 23.8°C P = 742.4 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
3	2.90	2.90	2.51	2.80	2.80	2.43
6	6.30	3.40	2.95	6.10	3.30	2.87*
9	10.00	3.70	3.21*	9.50	3.40	2.95*
12	13.60	3.60	3.12*	12.80	3.30	2.87*
15	17.20	3.60	3.12*	16.10	3.30	2.87*
18	20.80	3.60	3.12*	19.40	3.30	2.87*
21	24.30	3.50	3.03*	22.70	3.30	2.87*
24	27.80	3.50	3.03*	26.00	3.30	2.87*
27	31.20	3.40	2.95*	29.30	3.30	2.87*
30	34.80	3.60	3.12*	32.60	3.30	2.87*
Ave. Rate (ml/min)			1.029			0.960

* Values averaged to get average maximum rate.

TABLE LXXVIII

Dissolution of Hf Metal in 0.300 N HF and H_2SO_4 Acid Mixture at 25°C.

	Run No. 1 0.00 N H_2SO_4 T = 26.4°C P = 736.8 mm Hg			Run No. 2 0.50 N H_2SO_4 T = 27.1°C P = 733.8 mm Hg			Run No. 3 1.00 N H_2SO_4 T = 25.4°C P = 734.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--	0.00	--	--
3	1.50	1.50	1.27	1.80	1.80	1.52	1.70	1.70	1.45
6	3.90	2.40	2.04*	4.40	2.60	2.19*	4.20	2.50	2.13*
9	6.30	2.40	2.04*	6.80	2.40	2.02*	6.80	2.60	2.21*
12	8.70	2.40	2.04*	9.30	2.50	2.11*	9.30	2.50	2.13*
15	11.20	2.50	2.12*	11.80	2.50	2.11*	12.00	2.70	2.30*
18	13.50	2.30	1.95*	14.50	2.70	2.27*	14.40	2.40	2.04*
21	16.00	2.50	2.12*	16.90	2.40	2.02*	17.00	2.60	2.21*
24	18.40	2.40	2.04*	19.50	2.60	2.19*	19.50	2.50	2.13*
27	20.70	2.30	1.95*	22.00	2.50	2.11*	22.00	2.50	2.13*
30	23.10	2.40	2.04*	24.50	2.50	2.11*	24.50	2.50	2.13*
Ave. Rate (ml/min)			0.679			0.708			0.719

* Values averaged to get average maximum rate.

TABLE LXXIX

Dissolution of Hf Metal in 0.300 N HF and H_2SO_4 Acid Mixture at 25°C.

	Run No. 4 2.00 N H_2SO_4 T = 24.0°C P = 744.3 mm Hg			Run No. 5 4.00 N H_2SO_4 T = 23.6°C P = 735.0 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	--	--	0.00	--	--
3	2.00	2.00	1.74	2.10	2.10	1.81
6	4.60	2.60	2.26	4.60	2.50	2.15*
9	7.20	2.60	2.26	7.10	2.50	2.15*
12	9.70	2.50	2.17	9.60	2.50	2.15*
15	12.40	2.70	2.35	12.10	2.50	2.15*
18	14.90	2.50	2.17	14.60	2.50	2.15*
21	17.50	2.60	2.26	17.10	2.50	2.15*
24	20.00	2.50	2.17	19.60	2.50	2.15*
27	22.60	2.60	2.26	22.10	2.50	2.15*
30	25.10	2.50	2.17	24.60	2.50	2.15*
Ave. Rate (ml/min)			0.743			0.717

* Values averaged to get average maximum rate.

TABLE LXXX

Dissolution of Hf Metal in 0.300 N HF and H_2SO_4 Acid Mixture at 25°C.

	Run No. 6 6.00 N H_2SO_4 T = 24.0°C P = 734.8 mm Hg			Run No. 7 8.00 N H_2SO_4 T = 23.0°C P = 735.2 mm Hg		
Time	Vol	dV	dV STP	Vol	dV	dV STP
min	ml	ml	ml	ml	ml	ml
0	0.00	—	—	0.00	—	—
3	2.50	2.50	2.15*	2.70	2.70	2.33*
6	5.00	2.50	2.15*	5.20	2.50	2.16*
9	7.50	2.50	2.15*	7.60	2.40	2.07*
12	10.00	2.50	2.15*	10.00	2.40	2.07*
15	12.50	2.50	2.15*	12.40	2.40	2.07*
18	15.00	2.50	2.15*	14.80	2.40	2.07*
21	17.50	2.50	2.15*	17.20	2.40	2.07*
24	20.00	2.50	2.15*	19.70	2.50	2.16*
27	22.50	2.50	2.15*	22.10	2.40	2.07*
30	25.00	2.50	2.15*	24.50	2.40	2.07*
Ave. Rate (ml/min)			0.717			0.705

* Values averaged to get average maximum rate.

TABLE LXXXI

Difference Effect for the Dissolution of Hf Metal in 0.100 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 1
T = 28.3°C
P = 733.3 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	6.00	—	—	—				
10	8.00	2.00	167	0				
20	10.00	2.00	167	0				
30	11.00	1.00	84	10.2				
40	12.60	1.60	134	10.2				
50	14.00	1.40	117	10.2	163	112	71	122
60	15.90	1.90	159	0				
70	17.90	2.00	167	0				
80	19.40	1.50	125	7.6				
90	21.00	1.60	134	7.6	163	130	53	86
100	22.90	1.90	159	0				
110	24.50	1.60	134	5.6				
120	26.10	1.60	134	5.6	163	134	39	68
130	28.10	2.00	167	0				
140	30.10	2.00	167	0				
150	31.90	1.80	150	4.0				
160	33.70	1.80	150	4.0	167	150	28	45
170	35.70	2.00	167	0				

TABLE LXXXII

Difference Effect for the Dissolution of Hf Metal in 0.200 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 2
T = 30.6°C
P = 736.1 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	6.10	--	--	--				
10	10.40	4.30	356	0				
20	14.90	4.50	373	0				
30	18.90	4.00	331	5.4				
40	23.10	4.20	348	5.4	368	340	38	66
50	27.50	4.40	364	0				
60	32.00	4.50	373	0				
70	36.20	4.20	348	9.7				
80	40.30	4.10	339	9.7	368	344	68	92
90	44.70	4.40	364	0				
100	49.00	4.30	356	0				
110	52.80	3.80	315	16.0				
120	56.50	3.70	306	16.0	349	310	112	151
130	60.60	4.10	339	0				
140	64.60	4.00	331	0				
150	67.60	3.00	248	24.0				
160	70.50	2.90	240	24.0	323	244	167	246
170	74.30	3.80	315	0				
180	78.50	4.20	348	0				

TABLE LXXXIII

Difference Effect for the Dissolution of Hf Metal in 0.300 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 3
T = 30.0°C
P = 733.2 mm Hg

Time	Vol	dV	dV STP	I	dV_l	dV_t	6.97 I	Δ
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	6.30	—	—	—				
5	9.90	3.60	596	0				
10	13.50	3.60	596	0				
15	16.80	3.30	546	18.0				
20	20.30	3.50	579	18.0	620	562	125	183
25	24.20	3.90	645	0				
30	28.00	3.80	629	0				
35	31.30	3.30	546	25.5				
40	34.70	3.40	563	25.5	629	554	178	253
45	38.50	3.80	629	0				
50	42.20	3.70	612	0				
55	45.10	2.90	480	42.5				
60	47.70	2.60	430	42.5	604	455	210	359
65	51.30	3.60	596	0				
70	54.90	3.60	596	0				
75	57.40	2.50	414	11.4				
80	60.80	3.40	563	11.4	612	563	79	128
85	64.60	3.80	629	0				
90	68.10	3.50	579	0				
95	71.50	3.40	563	7.3				
100	74.80	3.30	546	7.3	579	554	51	76
105	78.30	3.50	579	0				
110	81.80	3.50	579	0				

TABLE LXXXIV

Difference Effect for the Dissolution of Hf Metal in 0.400 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 4
T = 31.3°C
P = 739.2 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	7.00	--	--	--				
4	10.90	3.90	807	0				
8	14.80	3.90	807	0				
12	18.40	3.60	745	27.0				
16	22.10	3.70	766	27.0	828	756	188	260
20	26.20	4.10	849	0				
24	30.50	4.30	890	0				
28	34.10	3.60	745	40.0				
32	37.60	3.50	724	40.0	880	734	279	425
36	41.80	4.20	869	0				
40	45.80	4.00	828	0				
44	49.20	3.40	704	53.0				
48	52.60	3.40	704	53.0	839	704	369	504
52	56.70	4.10	849	0				
56	60.70	4.00	828	0				
60	63.10	3.10	--	--				
64	66.20	3.10	642	55.0				
68	69.40	3.20	662	55.0	849	652	383	580
72	73.60	4.20	869	0				
76	77.80	4.20	869	0				
80	80.80	3.00	621	58.0				
84	83.90	3.10	642	56.0	849	632	397	614
88	87.90	4.00	828	0				
88	8.00	--	--	--				
92	12.00	4.00	828	0				
96	15.70	3.70	766	13.5				
100	19.50	3.60	745	13.5	849	756	94	187
104	23.70	4.20	869	0				
108	27.90	4.20	869	0				
112	31.70	3.80	787	9.5				
116	35.60	3.90	807	9.5				
120	39.50	3.90	807	9.5	859	800	66	125
124	43.60	4.10	849	0				
128	47.60	4.00	828	0				

TABLE LXXXV

Difference Effect for the Dissolution of Hf Metal in 0.500 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 5
T = 32.0°C
P = 739.0 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	6.50	--	--	--				
3	10.50	4.00	1099	0				
6	14.40	3.90	1071	0				
9	17.90	3.50	961	38.0				
12	21.70	3.80	1044	38.0	1099	1002	265	362
15	25.80	4.10	1126	0				
18	29.90	4.10	1126	0				
21	33.60	3.70	1016	45.5				
24	37.40	3.80	1044	45.5	1140	1030	317	427
27	41.60	4.20	1154	0				
30	45.70	4.10	1126	0				
33	49.20	3.50	961	59.0				
36	52.70	3.50	961	59.0	1126	961	411	576
39	56.80	4.10	1126	0				
42	61.10	4.30	1181	0				
45	64.60	3.50	961	71.0				
48	67.80	3.20	879	71.0	1154	920	495	729
51	71.90	4.10	1126	0				
54	76.00	4.10	1126	0				
57	79.00	3.00	824	79.0				
60	82.10	3.10	852	79.0	1126	838	551	839
63	86.20	4.10	1126	0				
63	6.30	--	--	--				
66	10.30	4.00	1099	0				
69	14.20	3.90	1071	0				
72	16.30	2.10						
75	19.90	3.60	989	30.0				
78	23.80	3.90	1071	30.0	1085	1030	209	264
81	27.80	4.00	1099	0				
84	31.90	4.10	1126	0				

TABLE LXXXVI

Difference Effect for the Dissolution of Hf Metal in 0.600 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 6
T = 30.6°C
P = 738.1 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	7.00	--	--	—				
3	12.00	5.00	1384	0				
6	17.20	5.20	1439	0				
9	22.00	4.80	1328	37.0				
12	26.90	4.90	1356	37.0	1480	1342	258	396
15	32.40	5.50	1522	0				
18	37.70	5.30	1467	0				
21	42.80	5.10	1411	47.0				
24	47.90	5.10	1411	47.5	1480	1411	329	398
27	53.30	5.40	1494	0				
30	58.60	5.30	1467	0				
33	63.50	4.90	1356	61.0				
36	68.20	4.70	1300	61.0	1480	1328	425	577
39	73.60	5.40	1494	0				
42	79.00	5.40	1494	0				
45	83.80	4.80	1328	74.0				
48	88.50	4.70	1300	74.0	1508	1314	516	710
51	94.00	5.50	1522	0				
51	6.00	--	--	—				
54	11.40	5.40	1494	0				
57	16.00	4.60	1273	82.5				
60	20.80	4.80	1328	82.5	1494	1301	575	768
63	26.20	5.40	1494	0				
66	31.70	5.50	1522	0				
69	36.30	4.60	1273	92.5				
72	41.00	4.70	1300	92.5	1508	1286	645	867
75	46.40	5.40	1494	0				
78	51.80	5.40	1494	0				
81	56.00	4.20	1162	108.0				
84	60.30	4.30	1190	108.5	1494	1176	756	1074
87	65.70	5.40	1494	0				
90	71.00	5.30	1467	0				

TABLE LXXXVII

Difference Effect for the Dissolution of Hf Metal in 0.700 N HF and 1.00 N HCl Acid Mixture at 25°C.

Run No. 7
T = 29.2°C
P = 737.4 mm Hg

Time	Vol	dV	dV STP	I	dV_1	dV_t	6.97 I	△
min	ml	ml	$\frac{mm^3}{cm^2 min}$	$\frac{ma}{cm^2}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$	$\frac{mm^3}{cm^2 min}$
0	6.00	--	--	--				
2	9.60	3.60	1505	0				
4	13.30	3.70	1547	0				
6	16.80	3.50	1463	0				
8	19.90	3.10	1296	55.0				
10	23.00	3.10	1296	55.0				
12	26.20	3.20	1338	55.0	1505	1310	383	578
14	29.90	3.70	1547	0				
16	33.70	3.80	1589	0				
18	37.40	3.70	1547	0				
20	40.60	3.20	1338	64.5				
22	43.90	3.30	1380	64.5				
24	47.00	3.10	1296	64.5	1547	1338	450	659
26	50.70	3.70	1547	0				
28	54.50	3.80	1589	0				
30	58.20	3.70	1547	0				
32	61.30	3.10	1296	77.5				
34	64.50	3.20	1338	77.0				
36	67.60	3.10	1296	77.0	1568	1310	637	895
38	71.40	3.80	1589	0				
40	75.00	3.60	1505	0				
42	78.80	3.80	1589	0				

TABLE LXXXVIII

Dissolution Potential of Hf Electrode in Hydrofluoric Acid at 25°C.

	Run No. 1 0.050 N HF		Run No. 2 0.100 N HF		Run No. 3 0.200 N HF	
Time	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.0608	0.7806	1.0730	0.7928	1.0921	0.8119
5	1.0596	0.7794	1.0721	0.7919	1.0798	0.7996
10	1.0602	0.7800	1.0631	0.7829	1.0735	0.7933
15	1.0591	0.7789	1.0603	0.7801	1.0704	0.7902
20	1.0581	0.7779	1.0603	0.7801	1.0695	0.7893
25	1.0583	0.7781	1.0602	0.7802	1.0675	0.7873
30	1.0572	0.7770	1.0601	0.7799	1.0661	0.7859
35	1.0570	0.7768	1.0604	0.7802	1.0677	0.7875
40	1.0558	0.7756	1.0613	0.7811	1.0677	0.7875
45	1.0551	0.7749	1.0616	0.7814	1.0671	0.7869
50	1.0549	0.7747	1.0616	0.7814	1.0661	0.7859
55	1.0548	0.7746	1.0616	0.7814	1.0660	0.7858
60	1.0545	0.7743	1.0598	0.7796	1.0664	0.7862
65	1.0548	0.7746	1.0598	0.7796	1.0660	0.7858
70	1.0533	0.7731	1.0596	0.7794	1.0656	0.7854
75	1.0533	0.7731	1.0598	0.7796	1.0656	0.7854
80	1.0529	0.7727	1.0598	0.7796	1.0640	0.7838
85	1.0533	0.7731	1.0597	0.7795	1.0643	0.7841
90	1.0530	0.7728	1.0597	0.7795	1.0643	0.7841
95	1.0535	0.7733	1.0597	0.7795	1.0630	0.7828
100	1.0530	0.7728	1.0603	0.7801	1.0640	0.7838
105	1.0533	0.7731	1.0606	0.7804	1.0634	0.7832
110	1.0528	0.7726	1.0606	0.7804	1.0621	0.7819
115	1.0529	0.7727	1.0610	0.7808	1.0625	0.7823
120	1.0531	0.7729	1.0615	0.7813	1.0615	0.7813

TABLE LXXXIX

Dissolution Potential of Hf Electrode in Hydrofluoric Acid at 25°C.

Time	Run No. 4 0.300 N HF Potentiometer Reading	$-E_{Hf}$	Run No. 5 0.400 N HF Potentiometer Reading	$-E_{Hf}$	Run No. 6 0.500 N HF Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	—	—	—	—	—	—
1	1.1042	0.8240	1.1211	0.8409	—	—
5	1.0912	0.8110	1.1085	0.8283	1.1317	0.8515
10	1.0875	0.8073	1.1028	0.8226	1.1265	0.8463
15	1.0833	0.8031	1.1002	0.8200	1.1223	0.8421
20	1.0807	0.8005	1.0986	0.8184	1.1144	0.8342
25	1.0845	0.8043	1.0985	0.8184	1.1161	0.8359
30	1.0798	0.7996	1.0978	0.8176	1.1138	0.8336
35	1.0796	0.7994	1.0941	0.8139	1.1122	0.8320
40	1.0794	0.7992	1.0921	0.8119	1.1118	0.8316
45	1.0778	0.7976	1.0902	0.8100	1.1075	0.8273
50	1.0783	0.7981	1.0915	0.8113	1.1049	0.8247
55	1.0775	0.7973	1.0918	0.8116	1.1041	0.8239
60	1.0772	0.7970	1.0912	0.8110	1.1043	0.8241
65	1.0765	0.7963	1.0908	0.8106	1.0918	0.8116
70	1.0769	0.7967	1.0919	0.8117	1.0980	0.8178
75	1.0770	0.7968	1.0903	0.8101	1.0960	0.8158
80	1.0762	0.7960	1.0886	0.8084	1.0920	0.8118
85	1.0767	0.7965	1.0913	0.8111		
90	1.0770	0.7968	1.0895	0.8093		
95	1.0768	0.7966	1.0884	0.8082		
100	1.0762	0.7960	1.0885	0.8083		
105	1.0770	0.7968	1.0877	0.8075		
110	1.0758	0.7956	1.0877	0.8075		
115	1.0748	0.7946	1.0874	0.8072		
120	1.0756	0.7954	1.0866	0.8064		

TABLE XC

Dissolution Potential of Hf Electrode in 0.300 N HF and HCl Acid Mixture at 25°C.

Time	Run No. 1 0.00 N HCl Potentiometer Reading	$-E_{Hf}$	Run No. 2 0.25 N HCl Potentiometer Reading	$-E_{Hf}$	Run No. 3 0.50 N HCl Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.1044	0.8242	1.0950	0.8148	1.0885	0.8083
5	1.0928	0.8126	1.0789	0.7987	1.0698	0.7896
10	1.0918	0.8116	1.0724	0.7922	1.0639	0.7837
15	1.0890	0.8088	1.0691	0.7889	1.0595	0.7793
20	1.0893	0.8091	1.0681	0.7879	1.0576	0.7774
25	1.0879	0.8077	1.0636	0.7834	1.0563	0.7761
30	1.0874	0.8072	1.0671	0.7869	1.0554	0.7752
35	1.0855	0.8053	1.0663	0.7861	1.0547	0.7745
40	1.0849	0.8047	1.0657	0.7855	1.0542	0.7740

TABLE XCI

Dissolution Potential of Hf Electrode in 0.300 N HF and HCl Acid Mixture at 25°C.

	Run No. 4 1.00 N HCl		Run No. 5 1.50 N HCl		Run No. 6 2.00 N HCl	
Time	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.0820	0.8018	1.0846	0.8042	1.0861	0.8059
5	1.0738	0.7936	1.0713	0.7911	1.0740	0.7938
10	1.0690	0.7888	1.0643	0.7841	1.0654	0.7852
15	1.0655	0.7853	1.0601	0.7799	1.0613	0.7811
20	1.0632	0.7830	1.0570	0.7768	1.0600	0.7798
25	1.0622	0.7820	1.0565	0.7763	1.0588	0.7786
30	1.0618	0.7816	1.0562	0.7760	1.0581	0.7779
35	1.0603	0.7801	1.0555	0.7753	1.0580	0.7778
40	1.0590	0.7788	1.0545	0.7742	1.0573	0.7771

TABLE XCII

Dissolution Potential of Hf Electrode in 0.300 N HF Acid at 25°C with Fluoride Salt Addition.

Time	Run No. 1 0.150 M NaF Potentiometer Reading	$-E_{Hf}$	Run No. 2 0.700 M KF Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts
0	—	—	—	—
1	1.1138	0.8336	1.1033	0.8231
5	1.1020	0.8218	1.0922	0.8120
10	1.0950	0.8148	1.0877	0.8075
15	1.0934	0.8132	1.0858	0.8056
20	1.0904	0.8102	1.0849	0.8047
25	1.0883	0.8081	1.0847	0.8045
30	1.0868	0.8066	1.0840	0.8038
35	1.0853	0.8051	1.0837	0.8035
40*	1.0848	0.8046	1.0838	0.8036
41	1.2623	0.9821	1.4465	1.1663
45	1.2642	0.9840	1.4561	1.1759
50	1.2625	0.9827	1.4604	1.1802
55	1.2582	0.9780	1.4472	1.1670
60	1.2493	0.9691	1.4327	1.1525
65	1.2385	0.9583	1.4236	1.1434
70	1.2280	0.9478	1.4183	1.1381
75	1.2220	0.9418	1.4134	1.1332
80	1.2122	0.9320	1.4092	1.1290
85	1.2005	0.9203	1.4046	1.1244
90	1.1917	0.9115	1.4012	1.1210
95	1.1890	0.9088	1.3977	1.1175
100	1.1362	0.9060	1.3946	1.1144
105	1.1863	0.9061	1.3914	1.1113
110	1.1838	0.9061	1.3889	1.1087

* Added 1.890 gm of NaF to reaction mixture in Run No. 1.
Added 12.201 gm of KF to reaction mixture in Run No. 2.

TABLE XCIII

Dissolution Potential of Hf Electrode in 0.300 N HF Acid at 25°C with Fluoride Salt Addition.

Time	Run No. 3 6.00 M NH_4F Potentiometer Reading	$-E_{Hf}$	Run No. 4 0.900 N Li_2SO_4 Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts
0	--	--	--	--
1	1.1120	0.8318	1.1182	0.8380
5	1.1000	0.8198	1.1055	0.8253
10	1.0942	0.8140	1.0998	0.8196
15	1.0920	0.8140	1.0968	0.8166
20	1.0908	0.8106	1.0968	0.8166
25	1.0902	0.8100	1.0954	0.8152
30	1.0895	0.8093	1.0955	0.8153
35	1.0895	0.8093	1.0948	0.8146
40*	1.0892	0.8090	1.0944	0.8142
41	1.5112	1.2310	1.1308	0.8506
45	1.5640	1.2838	1.1320	0.8518
50	1.5600	1.2798	1.1318	0.8516
55	1.5569	1.2767	1.1315	0.8513
60	1.5505	1.2703	1.1315	0.8513
65	1.5482	1.2680	1.1313	0.8511
70	1.5447	1.2645	1.1311	0.8509
75	1.5419	1.2617	1.1306	0.8504
80	1.5397	1.2595	1.1306	0.8504
85	1.5377	1.2575	1.1304	0.8502
90	1.5360	1.2558	1.1298	0.8496
95	1.5357	1.2555	1.1294	0.8492
100	1.5350	1.2548	1.1290	0.8488
105	1.5337	1.2535	1.1287	0.8485
110	1.5335	1.2533	1.1282	0.8480

* Added 66.672 gm of NH_4F to reaction mixture in Run No. 3.
Added 17.275 gm of Li_2SO_4 to reaction mixture in Run No. 4.

TABLE XCIV

Dissolution Potential of Hf Electrode in 0.300 N HF Acid at 25°C with Noble Metal Addition.

Time	Run No. 1 0.00500 N $AuCl_3$ Potentiometer Reading	Run No. 1 $-E_{Hf}$	Run No. 2 0.00500 N $AgNO_3$ Potentiometer Reading	Run No. 2 $-E_{Hf}$	Run No. 3 0.00500 N $PtCl_4$ Potentiometer Reading	Run No. 3 $-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.1088	0.8286	1.1180	0.8378	1.1153	0.8351
5	1.0960	0.8158	1.1057	0.8255	1.1002	0.8200
10	1.0932	0.8130	1.1020	0.8218	1.0946	0.8144
15	1.0928	0.8126	1.0997	0.8195	1.0886	0.8084
20	1.0895	0.8093	1.0977	0.8175	1.0881	0.8079
25	1.0908	0.8106	1.0965	0.8163	1.0886	0.8084
30	1.0910	0.8108	1.0953	0.8151	1.0883	0.8081
35	1.0890	0.8088	1.0939	0.8137	1.0885	0.8083
40*	1.0887	0.8085	1.0931	0.8129	1.0885	0.8083
41	0.9725	0.6923	1.0922	0.8120	0.9846	0.7044
45	0.9756	0.6954	1.0912	0.8110	1.0175	0.7373
50	0.9720	0.6918	1.0917	0.8115	1.0465	0.7663
55	0.9710	0.6908	1.0912	0.8110	1.0517	0.7715
60	0.9780	0.6978	1.0903	0.8101	1.0623	0.7821
65	0.9705	0.6903	1.0904	0.8102	1.0695	0.7893
70	0.9705	0.6903	1.0889	0.8087	1.0723	0.7921
75	0.9662	0.6860	1.0886	0.8084	1.0747	0.7945
80	0.9660	0.6858	1.0878	0.8076	1.0734	0.7932
85	0.9670	0.6868	1.0870	0.8068	1.0737	0.7935
90	0.9630	0.6828	1.0865	0.8063	1.0729	0.7927
95	0.9722	0.6920	1.0859	0.8057	1.0728	0.7926
100	0.9703	0.6901	1.0853	0.8051	1.0724	0.7922
105	0.9765	0.6963	1.0845	0.8043	1.0727	0.7925
110	0.9723	0.6921	1.0830	0.8028	1.0723	0.7921

* Added 49.8 ml of 3.5 gm $AuCl_3$/liter solution to Run No. 1.
Added 3.0 ml of 0.50 N $AgNO_3$ solution to Run No. 2.
Added 0.75 ml of 0.500 M $PtCl_4$ solution to Run No. 3.

TABLE XCV

Dissolution Potential of Hf Electrode in 0.300 N HF and 1.00 N HCl Acid Mixture at 25°C with 0.005 N $PtCl_4$ Addition.

Time	Potentiometer Reading	$-E_{Hf}$
min	volts	volts
0	--	--
1	1.0820	0.8018
5	1.0738	0.7936
10	1.0690	0.7888
15	1.0655	0.7853
20	1.0632	0.7830
25	1.0622	0.7820
30	1.0618	0.7816
35	1.0603	0.7801
40*	1.0590	0.7788
41	1.0153	0.7351
45	1.0210	0.7408
50	1.0180	0.7378
55	1.0162	0.7360
60	1.0149	0.7347
65	1.0150	0.7348
70	1.0144	0.7342
75	1.0156	0.7354
80	1.0172	0.7370
85	1.0200	0.7398
90	1.0226	0.7424
95	1.0262	0.7460
100	1.0234	0.7432

*Added 0.75 ml of 0.500 M $PtCl_4$ soln.

TABLE XCVI

Dissolution Potential of Hf Electrode in 0.300 N HF Acid at 25°C with Oxidizing Agent Addition.

Time	Run No. 1 0.0529 N $KMnO_4$ Potentiometer Reading	$-E_{Hf}$	Run No. 2 0.0529 N $K_2Cr_2O_7$ Potentiometer Reading	$-E_{Hf}$	Run No. 3 0.0529 N $NaBiO_3$ Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.1256	0.8454	1.1248	0.8446	1.1261	0.8459
5	1.1098	0.8296	1.1027	0.8225	1.1078	0.8276
10	1.1008	0.8206	1.0938	0.8136	1.0970	0.8168
15	1.0965	0.8163	1.0898	0.8096	1.0935	0.8133
20	1.0943	0.8141	1.0882	0.8080	1.0905	0.8103
25	1.0931	0.8129	1.0865	0.8063	1.0884	0.8082
30	1.0923	0.8121	1.0854	0.8052	1.0867	0.8065
35	1.0914	0.8112	1.0844	0.8042	1.0858	0.8056
40*	1.0906	0.8104	1.0835	0.8033	1.0845	0.8043
41	1.0936	0.8134	1.1255	0.8453	1.0872	0.8070
45	1.0993	0.8191	1.1284	0.8482	1.0728	0.7926
50	1.0995	0.8193	1.1278	0.8476	1.0505	0.7703
55	1.0990	0.8188	1.1270	0.8468	1.0236	0.7434
60	1.0983	0.8181	1.1270	0.8468	1.0150	0.7348
65	1.0968	0.8166	1.1275	0.8473	1.0060	0.7258
70	1.0968	0.8166	1.1275	0.8473	0.9950	0.7148
75	1.0962	0.8160	1.1273	0.8471	0.9760	0.6958
80	1.0950	0.8148	1.1270	0.8468	1.0070	0.7268
85	1.0945	0.8143	1.1260	0.8458	0.9840	0.7038
90	1.0936	0.8134	1.1259	0.8457	0.9680	0.6878
95	1.0928	0.8126	1.1260	0.8458	0.9750	0.6948
100	1.0912	0.8110	1.1255	0.8453	0.9750	0.6948
105	1.0897	0.8095	1.1255	0.8453	0.9570	0.6768
110	1.0880	0.8078	1.1250	0.8448	0.9490	0.6688

* Added 0.501 gm of $KMnO_4$ to reaction mixture in Run No. 1.
Added 1.556 gm of $K_2Cr_2O_7$ to reaction mixture in Run No. 2.
Added 2.220 gm of $NaBiO_3$ to reaction mixture in Run No. 3.

TABLE XCVII

Dissolution Potential of Hf Electrode in 0.300 N HF Acid at 25°C with Mineral Acid Addition.

	Run No. 1 0.100 N HCl		Run No. 2 0.100 N H_2SO_4		Run No. 3 0.100 N H_3PO_4	
Time	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$	Potentiometer Reading	$-E_{Hf}$
min	volts	volts	volts	volts	volts	volts
0	--	--	--	--	--	--
1	1.1243	0.8441	1.1229	0.8427	1.1127	0.8325
5	1.1080	0.8278	1.1147	0.8345	1.1005	0.8203
10	1.0993	0.8191	1.0933	0.8131	1.0908	0.8106
15	1.0932	0.8130	1.0907	0.8105	1.0896	0.8094
20	1.0903	0.8101	1.0862	0.8060	1.0873	0.8071
25	1.0890	0.8088	1.0838	0.8036	1.0865	0.8063
30	1.0899	0.8097	1.0838	0.8036	1.0850	0.8048
35	1.0903	0.8101	1.0843	0.8041	1.0843	0.8041
40*	1.0907	0.8105	1.0830	0.8028	1.0830	0.8028
41	1.0782	0.7980	1.0807	0.8005	1.0836	0.8034
45	1.0786	0.7984	1.0811	0.8009	1.0842	0.8040
50	1.0782	0.7980	1.0808	0.8006	1.0822	0.8020
55	1.0782	0.7980	1.0806	0.8004	1.0820	0.8018
60	1.0770	0.7968	1.0800	0.7998	1.0819	0.8017
65	1.0763	0.7961	1.0797	0.7995	1.0816	0.8014
70	1.0755	0.7953	1.0791	0.7989	1.0805	0.8003
75	1.0748	0.7946	1.0785	0.7983	1.0802	0.8000
80	1.0740	0.7938	1.0778	0.7976	1.0807	0.8005
85	1.0737	0.7935	1.0776	0.7974	1.0790	0.7988
90	1.0731	0.7929	1.0764	0.7962	1.0792	0.7990
95	1.0727	0.7925	1.0763	0.7961	1.0790	0.7988
100	1.0719	0.7917	1.0757	0.7955	1.0787	0.7985
105	1.0713	0.7911	1.0748	0.7946	1.0783	0.7981
110	1.0708	0.7906	1.0747	0.7945	1.0780	0.7978

* Added 2.65 ml of conc. hydrochloric acid to Run No. 1.
Added 0.85 ml of conc. sulfuric acid to Run No. 2.
Added 0.68 ml of conc. phosphoric acid to Run No. 3.

TABLE XCVIII

Dissolution Potentials of the Hf Electrode at Various Current Densities in HF Acid at 25°C.

Run No.	HF Conc.	Time	Current	Potentiometer Reading	$-E_{Hf}$
	equiv/l	min	amps	volts	volts
1	0.100	0	—	—	—
		5	0	1.0548	0.7746
		10	0	1.0495	0.7693
		12	5.3	0.5890	0.3088
		14	4.65	0.6467	0.3665
		16	3.90	0.7202	0.4400
		18	2.80	0.8104	0.5302
		20	1.95	0.8803	0.6001
		22	1.10	0.9594	0.6792
		24	0.85	0.9772	0.6970
		26	0	1.0473	0.7671
2	0.200	0	—	—	—
		5	0	1.0685	0.7883
		10	0	1.0657	0.7855
		13	8.0	0.6513	0.3711
		16	6.2	0.7388	0.4586
		18	4.75	0.8135	0.5333
		21	3.20	0.8957	0.6155
		23	1.50	0.9835	0.7033
		26	0	1.0578	0.7776
3	0.300	0	—	—	—
		5	0	1.0827	0.8025
		10	0	1.0775	0.7973
		13	10	0.6591	0.3789
		16	7.50	0.7622	0.4820
		19	5.70	0.8418	0.5616
		21	3.05	0.9550	0.6748
		23	1.60	1.0103	0.7301

APPENDIX E

APPENDIX E

I. CALCULATION OF DEVIATION FOR ACTIVATION ENERGIES

From the Arrhenius equation and the rate equation for the dissolution of hafnium in hydrofluoric acid (expressed in logarithmic form), we get:

$$\ln k = -E/RT + \ln A$$

$$= \ln (dV/dt) - \ln (HF)$$

where,

k = reaction rate constant

E = activation energy

R = gas constant

T = reaction temperature

A = frequency factor (constant)

dV/dt = average maximum hydrogen evolution rate for the dissolution of hafnium in hydrofluoric acid

(HF) = hydrofluoric acid concentration.

Therefore,

$$(-1/RT)\Delta E + (E/RT^2)\Delta T = \Delta(dV/dt)/dV/dt) - \Delta(HF)/(HF).$$

Numerical values to substitute into the equation are:

R = 1.99 cal/gmol.°K

T = 50°C = 323°K (The largest value for the reaction temperature is used so that the maximum error will be given, see Table IX, page 30.)

E = 5400 cal/gmol (Value of the experimentally determined activation energy from page 32.)

T = 1 C° = 1 K° (The water bath temperature was maintained within ± 0.1 C° of desired temperature, thus an allowance of 1 C° for the temperature variation should be more than sufficient.)

$\frac{\Delta(dV/dt)}{(dV/dt)}$ = 0.10 (Examination of the rate data, pages 125 to 156, shows that the usual deviations of the rates are five to seven per cent. Remembering that the rates used for the activation energy determinations were an average of many rates for several runs, the ten per cent allowed should be adequate.)

$\frac{\Delta(HF)}{(HF)}$ = 0.10 (The limiting case in this instance would be for 0.05 N hydrofluoric acid, which is about ten per cent ionized, see page 65. Using this error for all the concentrations would be very liberal.)

$$\frac{-\Delta E}{(1.99)(323)} + \frac{(5400)(1)}{(1.99)(323)^2} = 0.10 - 0.10$$

$\Delta E/643$ = 0.23 (Summing the absolute values.)

ΔE = (0.23)(643) = 148 cal = 0.15 kcal

The deviation, ± 0.1 kcal, for the activation energies should be a conservative estimation.

II. CALCULATION OF K FOR THE DIFFERENCE EFFECT ON HAFNIUM IN HYDROFLUORIC-1.00 N HYDROCHLORIC ACID MIXTURES

The data for these calculations are from Appendix D, pages 193 to 199, and are summarized in the first three columns of Table XCIX, this appendix, pages 216 and 217. The products and summations of the data for the least squares treatment have been made and are shown in the same table.

$$K' = \frac{\sum I_i \Delta_i}{\sum I_i^2} = \frac{873,571.00}{87,138.54} = 10.02$$

$$s^2_{I\Delta} = \frac{\sum(\Delta_i - bI_i)^2}{n-1} = \frac{\sum \Delta_i^2 - \frac{(\sum I_i \Delta_i)^2}{\sum I_i^2}}{n-1}$$

$$= \frac{8,806,671 - \frac{(873,571.00)^2}{87,138.54}}{36-1}$$

$$= \frac{8,806,671 - \frac{763,126,292,041}{87,138.54}}{35}$$

$$= \frac{8,806,671 - 8,757,621}{35} = \frac{49,050}{35} = 1,401$$

$$s_{I\Delta} = 37.431$$

$$t_{35,0.05} = 2.03$$

$$(\sum I_1^2)^{\frac{1}{2}} = (87,138)^{\frac{1}{2}} = 295.2$$

$$\epsilon = \frac{t_{35,0.05}\ S_{I\Delta}}{(\sum I_1^2)^{\frac{1}{2}}} = \frac{(2.03)(37.4)}{295}$$

$$= \frac{75.922}{295} = 0.257$$

$$K' - \epsilon < K < K' + \epsilon$$

$$10.02 - 0.26 < K < 10.02 + 0.26$$

$$9.76 < K < 10.28$$

Therefore, for 95% confidence interval,

$$K = 10.0 \pm 0.3.$$

TABLE XCIX

Calculation of K for the Difference Effect of Hf Metal Dissolving in Hydrofluoric-Hydrochloric Acid at 25°C by the Method of Least Squares.

Hf Conc	I	Δ	I^2	$I\Delta$	Δ^2
$\frac{\text{equiv}}{\text{l}}$	ma	$\frac{\text{mm}^3}{\text{cm}^2\text{-min}}$			
0.100	10.2	122	104.04	1,244.40	14,884
	7.6	86	57.76	653.60	7,396
	5.6	68	31.36	380.80	4,624
	4.0	45	16.00	180.00	2,025
0.200	5.4	66	29.16	365.40	4,356
	9.7	92	94.09	892.40	8,464
	16.0	151	256.00	2,416.00	22,801
	24.0	246	576.00	5,904.00	60,516
0.300	18.0	183	324.00	3,294.00	33,489
	25.5	253	650.25	6,451.50	64,009
	30.2	359	912.04	10,841.80	128,881
	11.4	128	129.96	1,459.20	16,384
	7.3	76	53.29	554.80	5,776
0.400	27.0	260	729.00	7,020.00	67,600
	40.0	425	1,600.00	17,000.00	180,625
	53.0	504	2,809.00	26,712.00	254,016
	55.0	580	3,025.00	31,900.00	336,400
	57.0	614	3,249.00	34,998.00	376,996
	13.5	187	182.25	2,524.50	34,969
	9.5	125	90.25	1,187.50	15,625
0.500	38.0	362	1,444.00	13,756.00	131,044
	45.5	427	2,070.25	19,428.50	182,329
	59.0	576	3,481.00	33,984.00	331,776
	71.0	729	5,041.00	51,759.00	531,441
	79.0	839	6,241.00	66,281.00	703,921
	30.0	264	900.00	7,920.00	69,696
0.600	37.0	396	1,369.00	14,652.00	156,816
	47.2	398	2,227.84	18,785.60	158,404
	61.0	577	3,721.00	35,197.00	332,929

TABLE XCIX

Calculation of K by the Method of Least Squares. (Continued)

Hf Conc	I	Δ	I^2	$I\Delta$	Δ^2
$\frac{\text{equiv}}{l}$	ma	$\frac{mm^3}{cm^2 min}$			
0.600	74.0	710	5,476.00	52,540.00	504,100
	82.5	768	6,806.25	63,360.00	589,824
	92.5	867	8,556.25	80,197.50	751,689
	108.5	1,074	11,772.25	116,529.00	1,153,476
0.700	55.0	578	3,025.00	31,790.00	334,084
	64.5	659	4,160.25	42,505.50	434,281
	77.0	895	5,929.00	68,915.00	801,025
Total			87,138.54	873,571.00	8,806,671

APPENDIX F

APPENDIX F

MOUNTING THE HAFNIUM SPECIMENS

Hafnium for this study was supplied in the form of crystal bars approximately one-half inch in diameter and three to five inches long. Specimens (disks) about 0.5 centimeter thick were obtained by making cross-sectional cuts along the bar. Because of the extreme toughness of the hafnium metal, it was very difficult to make cuts perpendicular to the longitudinal axis of the bar to obtain disks of uniform thickness. The most successful method employed consisted of placing the bar in a lathe and rotating it at low speed while sawing with a hack saw.

The surface of the specimen was polished and etched for about thirty seconds in 0.5 N hydrofluoric acid. If uneven etching was noted at the core (original hafnium filament used in the manufacturing process), the entire core was removed by drilling a hole through the specimen at that position. If no uneven etching was noted, the specimen was used without removing the core.

The edges of the disk were trimmed, giving the surface the shape of a square with an area of 1.00 ± 0.01 cm^2. A milling machine was used to trim the edges so that this accuracy was obtained without difficulty.

Specimen (Sample) for the Dissolution Rate Studies

The specimen was mounted in lucite with a Centermet press so that one square centimeter of surface area was exposed. The lucite mounting was trimmed making the edges and back around the hafnium specimen approximately one-eighth inch thick. Figure 29 shows a specimen mounted in lucite and attached to the PVC stirrer foot of the reaction apparatus.

Specimen (Electrode) for the Difference Effect and Dissolution Potential Studies

The specimen was mounted in lucite with a Centermet press so that one square centimeter of surface area was exposed. The lucite mounting was trimmed making three edges and the back around the hafnium specimen approximately one-eighth and one-fourth inch thick, respectively. The other edge, referred to later on as the top, was trimmed to a thickness of three-eighths inch. Holes were drilled in the lucite mounting from the top and back as shown in Figure 30 in order to attach a wire lead and glass-tube holder.

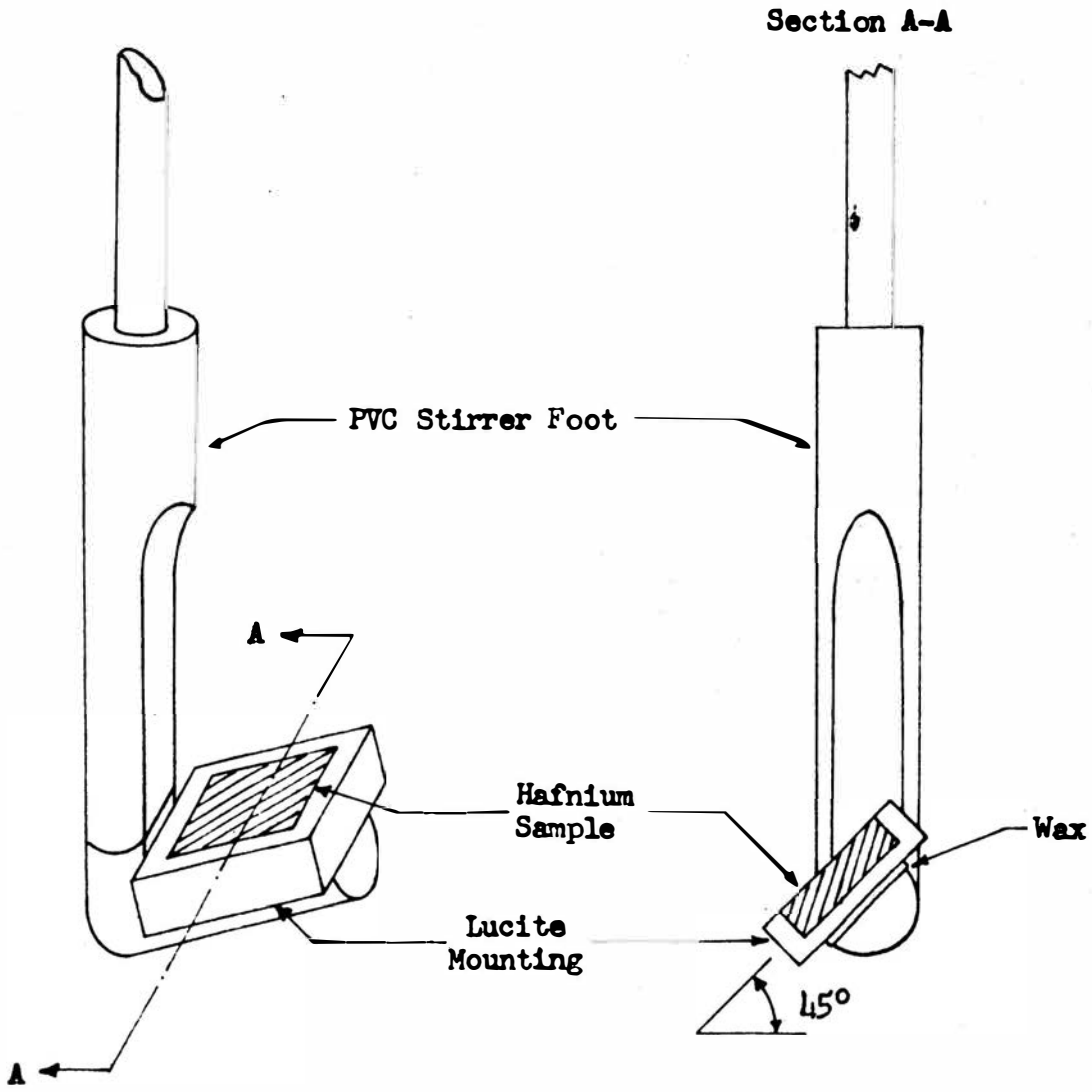

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Figure No. 29. Hafnium Sample Mounted on Polyvinyl Chloride Stirrer Foot for Dissolution Rate Studies.

SCALE: None	DATE 1-16-61	CASE NO:	
DRAWN BY: James N. Johnson		FILE NO:	
CHECKED BY:		FIGURE NO:	
APPROVED BY:		SHEET NO:	

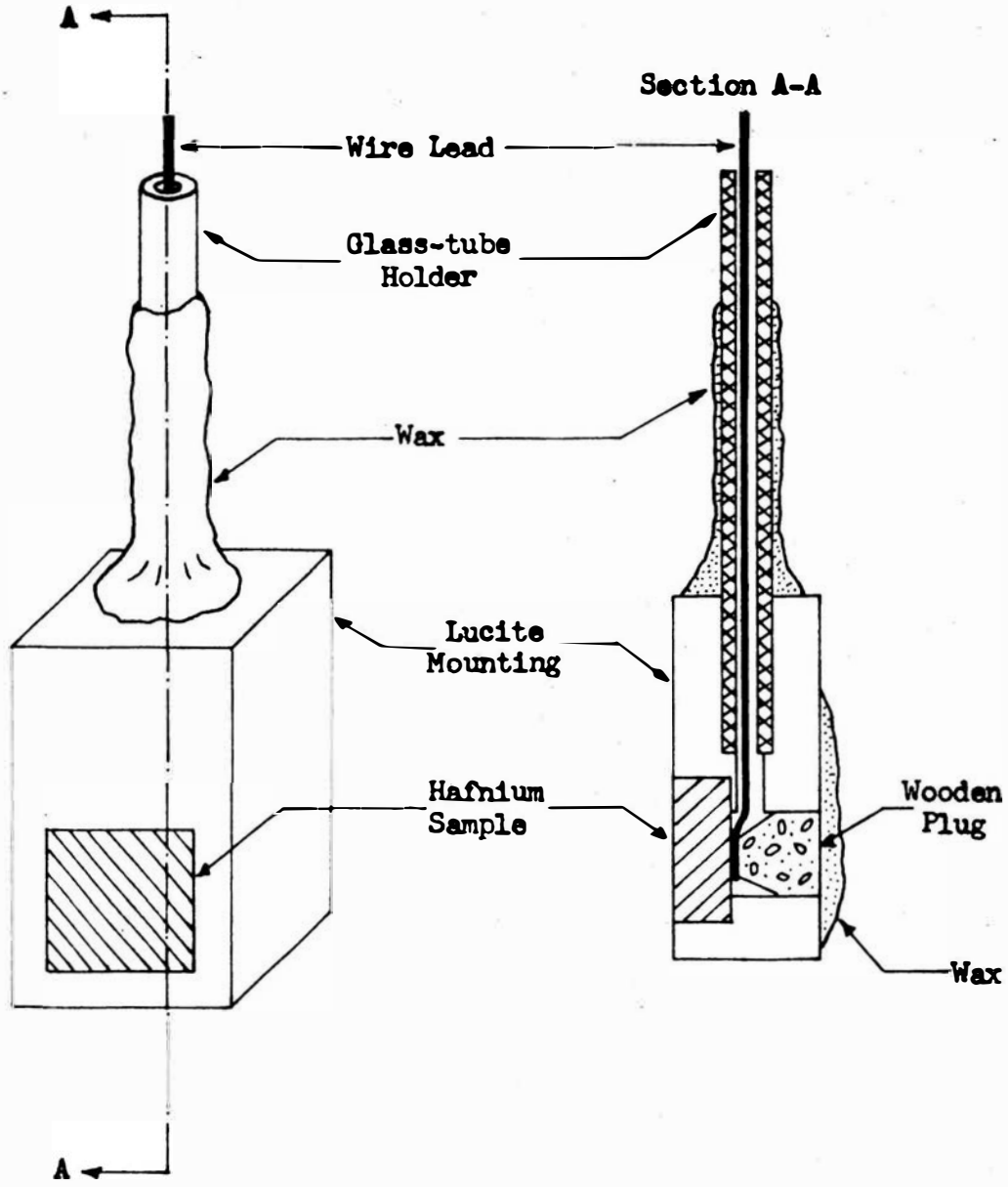

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Figure No. 30. Hafnium Electrode for Difference Effect and Dissolution Potential Studies.

SCALE: None	DATE 1-16-61	CASE	NO:
DRAWN BY: James W. Johnson		FILE	NO:
CHECKED BY:		FIGURE	NO:
APPROVED BY:		SHEET	NO:

APPENDIX G

APPENDIX G

SURFACE PREPARATION OF HAFNIUM SPECIMENS

The following procedure was used for the preparation of the hafnium metal surface of the samples used in the dissolution rate studies.

1. Remove the lucite-mounted sample from the PVC stirrer foot (see Figure 29, page 221).
2. Remove all the pits and etched places from the surface of the sample with a belt surfacer equipped with a No. 150 grit abrasive cloth belt. The sample should be dipped in water after each few seconds of grinding to prevent heating that would ruin the lucite mounting.
3. Finish the sample surface on a water-flushed four-stage hand grinder equipped with numbers 240, 320, 400, and 600 abrasive strips, proceeding from the coarsest to the finest. This operation should give a perfectly flat surface, containing no scratches, and appearing to be polished when examined by eye. This surface should be prevented from coming in contact with anything (especially the fingertips) that might leave a grease film.
4. Replace the hafnium sample on the PVC stirrer foot, attaching it with melted wax.

5. Etch the sample for about ten to twenty seconds (until hydrogen is being evolved from the entire metal surface) in hydrofluoric acid of the concentration to be used in the dissolution study. Rinse the sample with distilled water. The sample is now ready to be used for a rate determination.

Particular care should be taken to see that the lucite mounting fits tightly around the specimen edges. This prevents etching from changing the surface area. For this reason, the sample may have to be remounted from time to time.

Difference Effect Studies

The same procedure was used to prepare the surface of the hafnium electrode for use in the difference effect studies as is described above for the hafnium sample used in the dissolution rate studies. The lucite-mounted specimen was removed from the fixed glass-tube holder (see Figure 30, page 222) by breaking the wax seal and pulling the wire lead from the tube. Care must be taken not to allow water to enter the electrode during the surface preparation.

Dissolution Potential Studies

The same procedure was used to prepare the surface of the hafnium electrode for use in the dissolution potential studies as is described above for the hafnium sample used in the dissolution rate studies. The glass-tube holder is left on the electrode during the entire preparation. Care must be taken not to break the wax seals which would allow water to enter into the electrode.

VITA

James Winston Johnson was born May 25, 1930, in Quinton, Oklahoma. He attended the public schools in Clayton, Oklahoma, and graduated from high school in May, 1947.

In May, 1953, he received the degree of Bachelor of Science in Education with majors in mathematics and chemistry from Southeastern State College, Durant, Oklahoma. In July, 1953, he was inducted into the United States Army, and after two years of active duty, he was honorably released.

He enrolled in the Missouri School of Mines and Metallurgy, Rolla, Missouri, in September, 1955, and received the degrees of Bachelor of Science in Chemical Engineering in June, 1957, and Master of Science in Chemical Engineering in July, 1958.

He was an Instructor of Chemical Engineering at the Missouri School of Mines and Metallurgy from September, 1958, to August, 1960, during which time he worked toward the Doctor of Philosophy Degree in Chemical Engineering. He received a Cooperative Fellowship from the National Science Foundation, beginning in September, 1960, for the terminal year of work for the degree.